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Land management (specifically controlled heather burning) as a factor controlling carbon loss from upland peat soils

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Abstract

Peatlands contain a significant proportion of the worlds' total soil carbon, and are commonly assumed to serve as carbon sinks. There is however increasing evidence of carbon loss from peat soils, and DOC concentrations in UK rivers have increased markedly over the past three decades. Numerous drivers for increasing DOC release have been proposed but to date the potential role of land management has not been fully explored.

This study examines the potential effects of land management on DOC production and release from upland peat for a series of catchments in the South Pennines and North Yorkshire Moors. Spatial variability in drainage DOC concentration was examined in 50 small headwater catchments (<3 km^2) and nine reservoir catchments (1.5-21 km^2). A subset of the reservoir catchments was further examined through time to establish any relationship between land management and DOC.

Of the factors assessed, representing all combinations of soil type and land use, the proportion of new vegetation burn on blanket peat was consistently identified as the most significant predictor of spatial variation in DOC concentration. Significant relationships were identified between both temperature and sulphate deposition and longer-term DOC concentrations, but no interaction or cumulative effect of these two factors was shown. In contrast, the area of new burn on blanket peat explains more than twice the degree of variance in DOC over the same period. For catchments where no change in the area of new burn was determined, drainage DOC increases were minimal.

This study demonstrates that land management activities are important landscape-scale drivers of DOC concentration. Exposed peat surface following burning may be altering peat hydrology and improving conditions for microbial activity and enhanced DOC production. Land management therefore has significant consequence for water utilities facing increased costs of treatment and also for the conservation of blanket bog and blanket peat ecosystems currently managed by fire.

Acknowledgements

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Chapter 1. Introduction

1.1. Rationale

Soils contain more than twice the amount of carbon held in vegetation or the atmosphere (Batjes, 1996), with peat soils containing 20-30% of the world's (Gorham, 1991) and 50% of the UK's (Milne and Brown, 1997) total soil carbon. These soils therefore have a potentially significant role in both global and national carbon budgets, and are commonly assumed to act as net sinks for atmospheric carbon dioxide (e.g. Martikainen *et al*., 1995; Roehm and Roulet 2003). However, recent studies indicate that some UK peatlands are close to (Worrall *et al*., 2003a) or at best (e.g. Billet *et al*., 2004) carbon neutral. Carbon losses from peat soils in the UK are currently estimated to be more than 2% per year (Bellamy *et al*., 2005) and, although contended (e.g. Worrall and Burt, 2007), these estimates suggest that depletion of this storage may be occurring. Factors controlling soil carbon loss are of particular importance as they may act as positive feedback in global warming (Jenkinson *et al*., 1991; Smith and Shugart, 1993; Trumbore *et al*., 1996).

In addition to climatic concerns, high concentrations of dissolved organic carbon (DOC) in surface waters, in particular where these result from the presence of humic substances derived from peat decomposition (McDonald *et al*., 1991), have considerable implications for potable water supply, a key ecosystem service provided by upland areas. The organic colour imparted by humic substances (Aiken *et al*., 1985) represents a significant aesthetic issue for consumers and its removal is an increasing problem for water utilities. Upland water treatment works (WTWs) now combine multiple processes including coagulation, flocculation and clarification (Murray *et al*., 2007), which are not only expensive but create by-product disposal issues (Carlson *et al*., 2000). Incomplete removal of colour may also cause problems during disinfection processes, as humic substances react with chlorine to form potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Singer, 1999). Although coagulation with metal additives remains the preferred treatment, enhanced processes involving, for example, magnetic ion exchange (MIEX®) (Fearing *et al*., 2004) are being more frequently trialled to address the challenges of meeting legislative standards for THMs of 100 μg l^{-1} in drinking water (EU Drinking Water Directive 98/83/EC) caused by increasing levels of humic DOC (hDOC). Understanding the factors controlling DOC production within peat catchments is therefore important for long-term carbon cycling and planning water supply.

Upland catchments in the UK exhibit widespread variation in DOC production and release (e.g. Dawson *et al*., 2002; Monteith and Evans, 2005). Stream discharge (e.g. Grieve, 1984), and physical catchment characteristics including slope (Eckhardt and Moore, 1990; Aitkenhead *et al*., 1999; Andersson & Nyberg, 2008), altitude (Hope *et al*., 1997a) and percent cover of blanket or deep peat (McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001) have been shown to influence drainage DOC concentration. However, more localised differences in DOC release at variance with these observations have been found in many small upland catchments (Yallop *et al*., 2008) and increasing trends in DOC concentrations have also been observed in surface waters draining areas of upland peat (Freeman *et al*., 2001a; Worrall *et al*., 2003b; Evans *et al*., 2005). Numerous drivers of increased DOC production have been proposed, including hydrological (Evans *et al*., 2005) and climatic change (e.g. Freeman *et al*., 2001a), elevated atmospheric CO_2 levels (Freeman *et al*., 2004), and severe drought (Worrall and Burt, 2004). Decreasing atmospheric acid deposition has also been implicated (Evans *et al*., 2006) and this may be important as a driver of increases in DOC globally (Monteith *et al*., 2007). However, none of these factors appear obvious candidates to explain local or small-scale spatial variation in patterns of DOC release, a suggestion supported by observations of Worrall and Burt (2007) that DOC release from upland peat catchments does not correlate well with changes in either acid deposition or occurrences of severe drought.

In the UK, upland areas have a complex history of human occupation, land use and management, activities that do vary at fine spatial scales and could therefore provide potential localised drivers of environmental change, over and above those that may be occurring at a larger scale. Many areas of upland blanket peat, particularly in the English Pennines, were extensively drained in the 1960s and 1970s (Holden *et al*., 2004) and currently livestock grazing and controlled burning for red grouse *Lagopus lagopus* L. game shooting are the most extensive forms of land management (Simmons, 2003). The hydrological effects of drainage appear mixed, as earlier studies (Coulson *et al*., 1990; Stewart and Lance, 1991) suggest that artificial drains merely intercept surface flow and therefore only tend to affect water tables within a few metres of the channel. More recent work (Holden *et al*., 2006), however, suggests that increased drainage has cumulative effects that are significant in the long term and Wallage *et al*. (2006) identified higher interstitial DOC concentrations in drained peat catchments. To date there is little evidence to suggest that grazing has any direct effect on DOC although the consequences of burn management have been studied. Under well-managed rotational burns, interstitial DOC concentrations may be lower (Worrall *et al*., 2007), although accelerated surface erosion, increased infiltration and throughflow (Imeson, 1971), more extreme and variable temperatures (Fullen, 1983; McDonald *et al*., 1991), increased porosity (Mallik and Fitzpatrick, 1996) and reduced carbon sequestration (Garnett *et al*., 2000) have all been found on moorland under burning management. Although not quantified, Mitchell and McDonald (1992) noted higher colour in surface waters draining from catchments with extensive burning and Yallop *et al*. (2008) found a highly significant relationship between the extent of burn management on blanket peat and water colour (Hazen) in drainage waters.

1.2. Aim and objectives

The aim of the research presented in this thesis is to examine the potential effects of land use and management, in particular controlled burning of moorland, on DOC concentrations in surface waters draining upland peat catchments in the UK. A greater understanding of the influence of localised factors on spatial and temporal variation in DOC production and release from upland peat soils is timely, as changes in localised factors may result from changes in land management policy. This research focuses on upland regions in the South Pennines and the North Yorkshire Moors, and is constrained to areas of moorland that supply WTWs operated by Yorkshire Water.

Four objectives were defined to address the aim of this research:

1. categorise and define upland land use and management;

2. establish the effect of land use and management on drainage DOC concentrations from small headwater catchments sampled manually and for reservoir catchments using secondary data from utility water treatment works;
3. assess the influence of land use/management and extrinsic factors (including climate and acid-deposition) on DOC concentration in catchment drainage over the last 40 years;
4. determine DOC efflux for catchments examined in Objective 3 to quantify the amount of carbon that is removed from them via fluvial pathways, and the fraction that can be attributed to factors identified as influencing DOC production.

1.3. Thesis outline

The research undertaken in this thesis is placed in the context of previous and current related work in Chapter 2. Upland environments and associated soil types are reviewed, with particular focus given to the formation of blanket peats and processes that operate within these ecosystems. Products of decomposition that contribute to DOC and proposed drivers of enhanced peat decomposition are also discussed.

Image processing and land cover classification methods relevant to Chapters 5 to 8 and assessment of the errors associated with these techniques are presented in Chapter 3. This section addresses the first part of Objective 1 and presents categories of land use that will be used in land cover classification. Detailed methods of water sample analysis undertaken in Chapter 5, processing of water utility colour data used in Chapter 7 and commonly used statistical tests are also provided in Chapter 3.

Chapter 4 focuses on the second part of Objective 1 to define land management classes, and presents the results of a field-based survey of controlled management burns in summer 2005. Assessment of rates of vegetation regeneration, closure of canopy and exposure of peat surface in burn scars in relation to the time since a burn occurred are used to refine definitions of aerial photographic interpretion (API) burn classes given by Yallop *et al.* (2006). This information is key to interpretation of the main findings of this research.

The potential effects of land use and management activities on spatial variation in DOC concentration (Objective 2) are assessed in Chapters 5 and 6. Analysis is undertaken for a series of small headwater catchments sampled in the field (<3 km^2) and a number of reservoir catchments (1.5-22 km^2). The data presented in these two chapters include expansion of the results published in Yallop and Clutterbuck (2009). Land use, climate, acid deposition and drainage DOC concentrations for the last 40 years are reconstructed for a series of upland reservoir catchments in Chapter 7. These data are used to assess the influence of both extrinsic and intrinsic factors on DOC concentration over this period (Objective 3).

A rainfall-runoff model is developed in Chapter 8 and used to estimate runoff for the catchments examined in Chapter 7 for the period of data availability. Modelled runoff is then used to quantify DOC efflux and carbon loss from blanket peat for the upland catchments examined (Objective 4). Estimates of carbon loss derived in Chapter 8 highlight the significance of the work in Chapters 5 to 7. The results of this research and the implications of the key findings are discussed in Chapter 9.

Chapter 2: Literature review

2.1. Upland environments

Upland areas have been defined in geology as land that is at a higher elevation than the alluvial plain or stream terrace (Holmes, 1983). Globally these environments provide important ecosystem services, including the supply of potable water. Uplands typically receive greater precipitation than lowland areas and more mountainous zones may accumulate and store winter precipitation as snow or ice. This store can complement lower precipitation levels in summer with melt water (Viviroli and Weingartner, 2004). Climates are often more extreme in these regions with stronger winds, fewer sunshine days, higher rainfall and lower temperatures (Pearsall, 1950). The associated geomorphological processes mean uplands have great influence on downstream processes such as sedimentation (Labadz *et al*., 1995). Due to the remoteness and inaccessibility of some of these areas, they provide habitats where declining species such as the black grouse (*Tetrao tetrix*) are more able to survive (Simmons, 2003).

In Great Britain, uplands are typically considered to be areas above the upper limits of agricultural enclosure (around 250 - 400 m above sea level), although as the height of this limit varies geographically (Backshall *et al*., 2001), absolute altitudinal definitions can be inappropriate and constraining. Ratcliffe and Thompson (1988) do however offer guideline definitions of upland ground and estimates of the respective land surface cover in Britain (Table 2.2.1). The area covered by uplands and marginal uplands in the Countryside Survey 2000 (Haines-Young *et al*., 2000), are comparable to those given by Ratcliffe and Thompson (1988), accounting for 17% (2.6 million ha) of England and Wales and 25% (5.8 million ha) of Great Britain (Figure 2.1.1).

Table 2.1.1. Extent of upland ground in Britain (from Ratcliffe and Thompson, 1988).

Altitude (m)	Main land type	% Britain's surface	Area (km^2)			
			Britain	Scotland	England	Wales
123-244	Marginal agricultural	23.9	54,324	19,944	28,869	5,511
245-610	Hill pasture and moorland	20.8	47,315	27,030	12,363	7,922
611-914	Mountain range	2.3	5,263	4,645	394	224
>915	High mountains	0.2	402	394	2	6

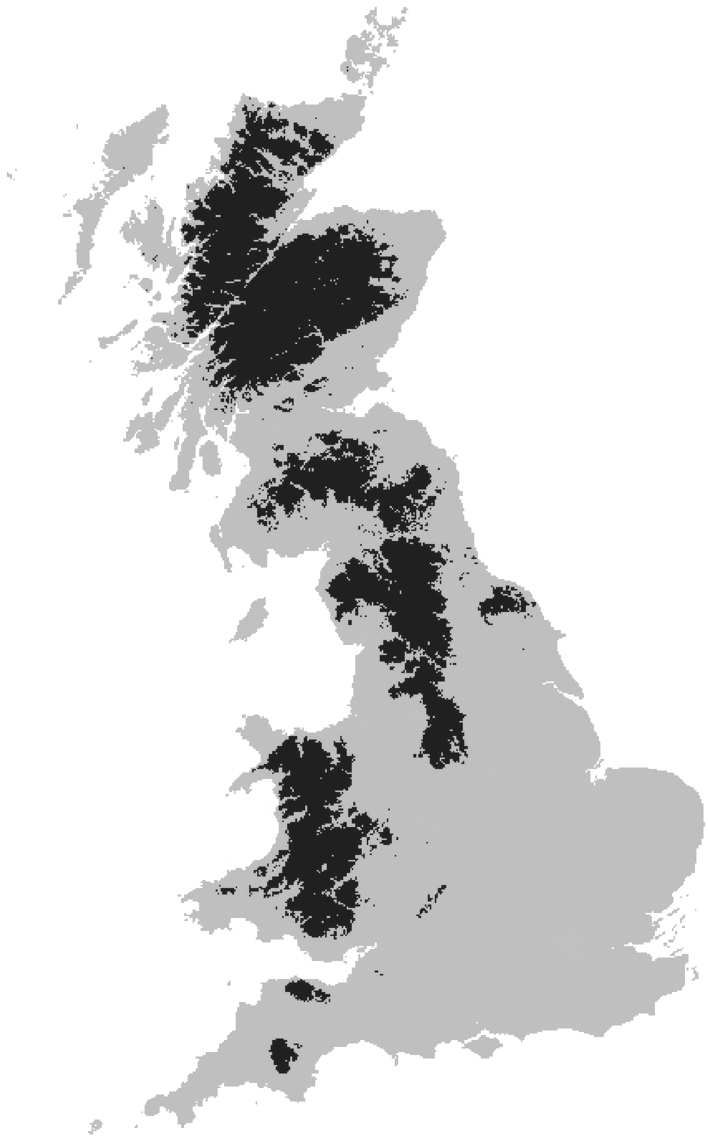


Figure 2.1.1. Location and extent of Environmental Zones 3 and 6, representing uplands and marginal uplands, in Countryside Survey 2000 (from Haines-Young *et al*., 2000).

The very presence of the uplands is indicative of harder rocks capable of withstanding the processes of weathering and erosion (for example the granites of Dartmoor and Millstone Grit series of the Pennines). Whilst the origins are inextricably linked to geological processes, much of the current topography can be attributed to periods of glaciation in the Pleistocene (Pearsall, 1950; Simmons, 2003), which terminated about 10,000 years ago. Current soils and vegetation, however, owe more to post-glacial climatic, geomorphic and anthropogenic activities. In the post glacial period (Holocene) initial warming of the climate led to the establishment of deciduous forest, which attained maximum treeline (around 700m) around 8000-7000 years ago (Birks, 1988; Simmons, 2003). The beginning of this period is also concurrent with the first evidence of humans (Simmons, 2003). Palaeoecological data suggests that extensive deforestation subsequently occurred from *c.* 4000-3000 years ago, and is suggested to be the result of a combination of human activity and a shift towards a more oceanic climate with higher precipitation and stronger winds (Birks, 1988; Simmons, 2003).

The contemporary upland landscape is dominated by heaths, bogs and rough grassland (Table 2.1.2), though in England and Wales there is a shift towards a greater dominance of improved grassland. Livestock grazing and controlled burning for red grouse (*Lagopus lagopus*) game shooting are probably the most extensive activities undertaken in these areas (Simmons, 2003), and are indicative of the continued human influence. In some locations linear features such as a wall or fence may accentuate the boundary between improved lowland grassland and rougher ‘upland’ vegetation, yet more commonly the lowlands and uplands merge through a broad band of transitional vegetation and land management (Backshall *et al*., 2001).

Table 2.1.2. Dominant upland habitats in Countryside Survey 2000 (Haines-Young *et al*., 2000).

Upland habitat	% GB upland	% E&W upland	% Scotland upland
Improved Grass	14.2	28.1	2.9
Conifer woodland	10.7	5.8	14.7
Bog	20.6	6.0	32.4
Dwarf shrub heath	19.1	16.1	21.6
Acid Grass	16.7	17.9	15.8

Prevailing winds from the Atlantic subject the British uplands to an oceanic climate that is not common elsewhere (Ratcliffe and Thompson, 1988). The climate is characterised by low temperatures, severe wind exposure, very high precipitation, cloud and humidity, persistent frost and snow cover and lack of sunshine (e.g. Pearsall 1950; Ratcliffe and Thompson, 1988; Simmons, 2003). Perhaps as a result of the climate, several internationally scarce habitats (Thompson *et al*, 1995), rare types of blanket bog (Ratcliffe and Thompson, 1988) and unique plant communities (Ratcliffe and Thompson, 1988) exist within the British uplands.

The British upland climate also has great influence on the soil types found in these regions. Pearsall (1950) considered upland soils as belonging to a developmental series ranging from skeletal/immature soils composed predominantly of rock fragments on mountain-tops, through brown earths under woodland and grassland, to podzols of varying porosity, waterlogged gley soils and blanket peats, which account for the majority of stable upland soils (Figure 2.1.2). As a result of the high precipitation, waterlogging occurs on sites with poor surface and sub-surface drainage (Curtis *et al*., 1976) and lower upland temperatures reduce biological activity. Slower breakdown of plant debris resulting from these conditions can lead to the accumulation of plant debris, and the formation of peat soils.

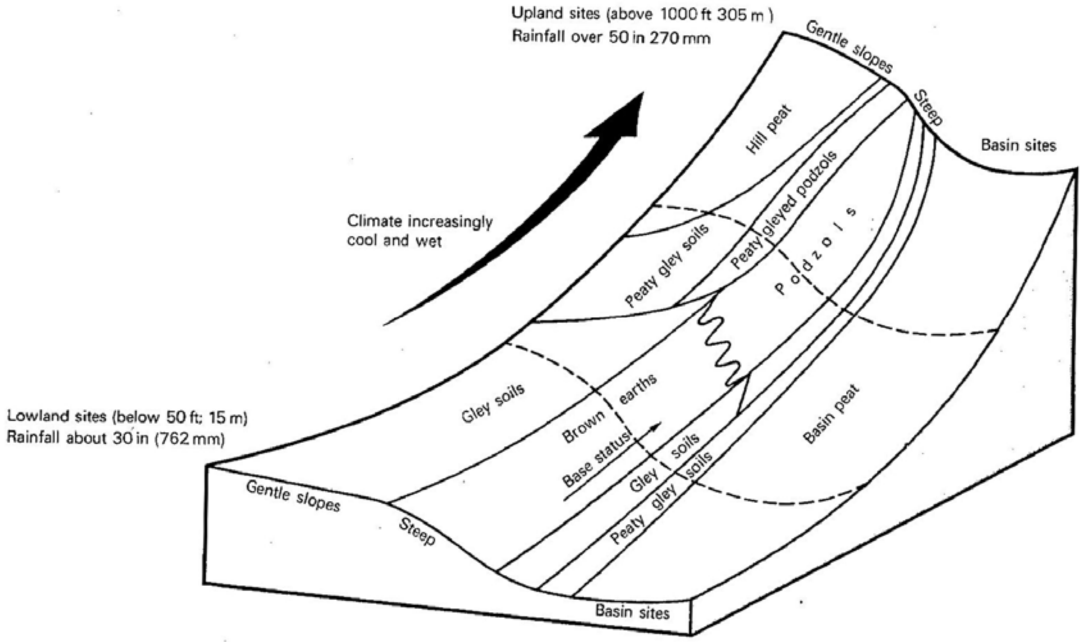


Figure 2.1.2. Transition of soils from lowland to upland areas in relation to climate and relief (from Curtis *et al*., 1976).

2.2. Peat

2.2.1. Peat description and ecosystem terminology

'Peat' is used to describe the accumulated remains of plant materials that have not decomposed. In boreal, arctic and subarctic regions, decomposing microbial activity is suppressed by waterlogging, while in tropical rainforest environments plant productivity may simply exceed the rate at which organisms can 'process' the material (Moore and Bellamy, 1974). Definitions of peat are, however, somewhat arbitrary; for example the Soil Survey of England and Wales (Burton and Hodgson, 1987) states that the deposit must be at least 30 cm deep, and contain more than 50 % organic matter. It has therefore been highlighted (Clymo, 1983) that there is no clear break in the continuum between a mineral soil with organic matter in it (such as the surface of a podzol) and an almost pure *Sphagnum* peat of which more than 99% is organic matter.

It is also noted (Immirzi *et al.*, 1992, Charman, 2002) that different countries and disciplines use the same vocabulary to describe or define peat ecosystems, but often with conflicting meaning. Table 2.2.1 provides a summary of these terms, the definitions of which will be adopted within this thesis.

Table 2.2.1. Common terminology used to describe peat ecosystems (from Immirzi *et al.*, 1992; Charman, 2002).

Term	Definition
Mire	The collective and internationally recognised term for all peat forming ecosystems
Peatland	The physiographic, geomorphological or biogeographic setting of peat. It is not synonymous with mire, because it includes areas which may no longer carry peat-forming communities
Wetland	A broader collective term which includes all active peat-forming habitats, but also non-peat-forming habitats
Fen	A mire which is influenced by water from outside its own limits
Bog	A mire which receives water solely from rain and/or snow

The origin of a mire (suffix 'genous) is described with reference to the water source at the time of formation. This may not reflect the present trophic status of a mire, as the water source may have since been altered by hydrological or biological transitions (Moore, 1995). **Ombrogenous** peatlands form where the sole source of water is atmospheric. In **geogenous** or **minerogenous** peatlands the atmospheric water source is complemented by other water from rocks or soils. These latter terms are further subdivided into **topogenous** where the water is static as a result of topographic position (e.g. basin/floodplain), **soligogenous** where the water is flowing, such as spring or sloping fen and **limnogenous** referring to water from lakes or rivers, such as lake shore.

Trophic status (suffix 'trophic') of mires is described with reference to the current water source. **Ombrotrophic** refers to bogs, which receive all their water and nutrients from the atmosphere and are therefore acid and low in plant nutrients. **Minerotrophic** or

rheotrophic refer to fens, which receive inputs from outside their confines, from groundwater or surface runoff. These therefore tend to be more nutrient-rich and alkaline. **Rheotrophic** is more commonly used when the water source is predominantly flowing. Fens are further categorized by their nutrient supply into **oligotrophic** (poorly-fed), **mesotrophic** (intermediate) and **eutrophic** (well-fed) mires (Charman, 2002).

2.2.2. Global significance of peat

Despite extensive studies of mires and peat, the creation of a global inventory (Figure 2.2.1) is problematic. Immirzi *et al*., (1992) estimate the total global peatland extent to be between 386 and 409 million ha, but note the following problems with the existing inventory data:

i. Variable detail, accuracy and reliability of areal estimates;
ii. Errors and variations in classification;
iii. Uncritical repetition and acceptance of others' estimates;
iv. Frequent omission of analytical data (e.g. depth of profile).

Peatlands represent a significant store of terrestrial carbon (e.g. Gorham, 1991; Jenkinson *et al*., 1991; Immirzi *et al*., 1992; Page *et al*., 2002) and are a key component of the global carbon cycle. Boreal and subarctic peatlands are estimated to contain one-third (455 Pg) of the total world pool of soil carbon (1395 Pg) (Gorham, 1991), and in Britain account for 50% of total soil carbon (Milne and Brown, 1997).

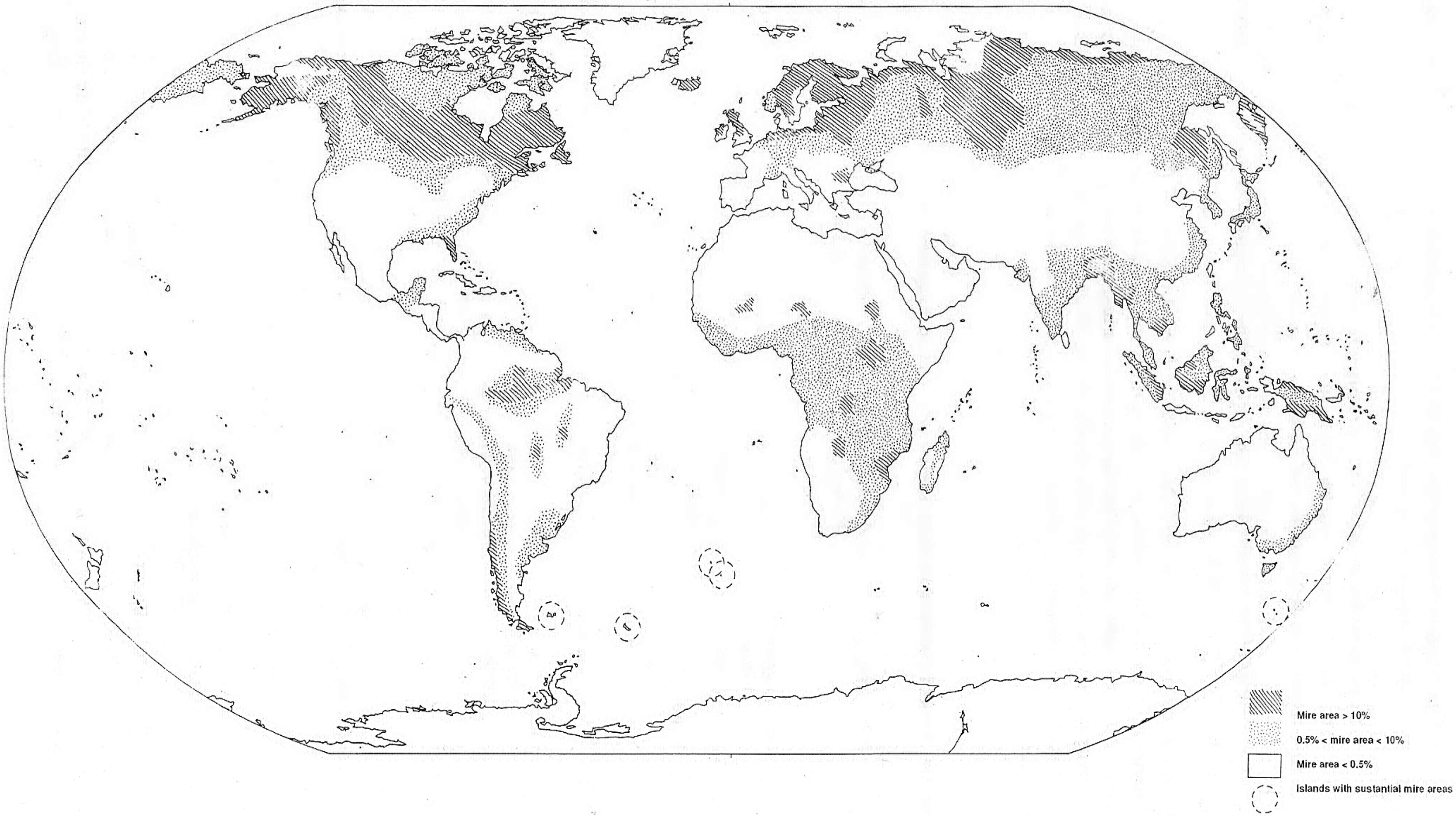


Figure 2.2.1. Global distribution of mires (from Immirzi *et al*., 1992).

2.2.3. Peat formation

The formation of peat is often referred to as a two stage process, namely ‘initiation’ and ‘accumulation’ (Moore, 1975; Charman 2002). Environmental change leading to waterlogging will promote peat initiation by suppressing microbial activity and slowing the rate of decay (Moore, 1975). This may be influenced by climate, geomorphology, geology and soils, biogeography and human activities (Charman, 2002).

The hydrological balance is influenced by climate, and a shift to a positive water balance (i.e. greater input of water than loss) as a result of climatic change (Steig, 1999) may be instrumental in peat initiation (Tallis, 1991). Topographically, basins will tend to collect water whilst hilltops and slopes are considered water-shedding, though in regions of high humidity peat can form on slopes up to 20° or more (Clymo, 1983). Impermeable substrates will also promote the collection of water, while geological faulting or hydrogeological features such as spring lines can increase water loss (Charman, 2002). In terms of biogeography, the presence of particular plants or groups of plants can increase the susceptibility of the area to peat development (Charman, 2002). Most peatlands have formed in the last 10,000 – 15,000 years in a period of major human advancement (Charman, 2002) and in some areas there is evidence that human influence on the hydrological balance may be closely linked with peat formation (Moore, 1975).

To describe the initiation phase some authors (e.g. Lindsay, 2003) adopt the early conceptual models of ‘terrestrialisation’ (Weber, 1902 cited in Lindsay, 2003) and ‘paludification’ (Cajander, 1913 cited in Lindsay, 2003). In terrestrialisation a water body becomes infilled with vegetation and organic matter until no open water remains and the site becomes peatland. Paludification was later proposed to explain how peat can form exterior to aquatic phases if the ambient conditions are suitably wet or if ground becomes wet due to adjacent waterlogging. Other authors (e.g. Immirzi *et al.*, 1992) prefer to use the concept of primary, secondary and tertiary peats proposed by Moore and Bellamy (1974). Primary peats, perhaps synonymous with terrestrialisation, form in depressions or basins and can form in most climates (Immirzi *et al.*, 1992). Secondary peats form on waterlogged ground adjacent to the basin, and are perhaps similar to a component of paludification. Tertiary peats develop independently of any groundwater, where vegetation is able to retain enough moisture to create its own water table.

Peat will accumulate when the rate of addition of organic matter exceeds the rate of decay. As peatification is a highly inefficient process, where typically less than 10% of plant production accumulates as peat (Killops and Killops, 1993), it can take millennia for a deposit that qualifies as peat (e.g. 30cm: Burton and Hodgson, 1987) to develop (Immirzi *et al.*, 1992). Most matter is added at the surface (particularly in the case of mosses), but rhizomes and roots of vascular plants may add matter up to 2 m depth (Clymo, 1983). To explain the dynamics of accumulating mires, a two-layer model (Table 2.2.2) was proposed by early 20th Century Russian scientists but Ingram (1978) renamed the layers acrotelm (upper layer) and catotelm (lower layer). Within this two-dimensional model, the boundary between the layers is essentially the maximum depth to which the water table drops in drier months. As a result, the acrotelm is periodically aerated, supporting both living vegetation and aerobically active microbes. As the rate of decay is affected by *inter alia* temperature and oxygen supply (Clymo, 1983) the model suggests that decomposition will occur at faster rates within this layer. Raising of the water table in wetter months facilitates the transport of the products of decay from the system. Decomposition continues in the catotelm, but with increasing burial depth acidity increases, bacterial communities change and their activities decrease and eventually cease (Killops and Killops, 1993). Archaeological finds of preserved human bodies such as the 2000 year old 'Lindow Man' are testimony to the slow rate of decay at depth. Water movement is also very much slower in this layer, and transport of any products of anaerobic decay will be slow.

Table 2.2.2. Main characteristics of the acrotelm (upper layer) and catotelm (lower layer) in peatlands (from Charman, 2002).

Character	Acrotelm (upper layer)	Catotelm (lower layer)
Water table	Fluctuating	Absent
Water content	Variable	Constant
Aeration	Periodically active	Anaerobic
Microbial activity	High with aerobic and anaerobic activity	Low with only anaerobic activity
Water movement	Relatively fast. Variable from surface to base	Very slow, constant
Exchange of energy and matter	Rapid	Slow

The popular diplotelmic model (Ingram, 1978) suggests that in pristine, accumulating mires decomposition of organic matter occurs predominantly in the acrotelm. This two-dimensional model also implies that most runoff and thus exchange of nutrients and DOC occurs in this layer. However, natural soil piping within blanket peats can significantly expand the area of a catchment (Jones, 2004), and perhaps account for up to 10% of runoff (Holden and Burt, 2003a). This indicates that water movement is not limited to the acrotelm, and there is a further profile of peat exposed to aeration and potential DOC production.

2.2.4. British upland peats

The majority of peatlands in upland Britain are ombrotrophic owing to the topography of these regions. These peatlands can be classified in terms of hydromorphology (Charman, 2002), and fall into three categories: raised mire/bog, intermediate mire/bog and blanket mire/bog (Figure 2.2.2).

Raised bogs have a distinctly convex profile 'dome' (Figures 2.2.2a and 2.2.3). The mire may have geogenous or minerogenous origins from initiation in a depression, but now receives water solely from atmospheric inputs due to its morphology. A ring of surrounding minerotrophic fen (Charman, 2002), sometimes referred to as 'lagg' fen (e.g. Lindsay, 2003), may still exist.

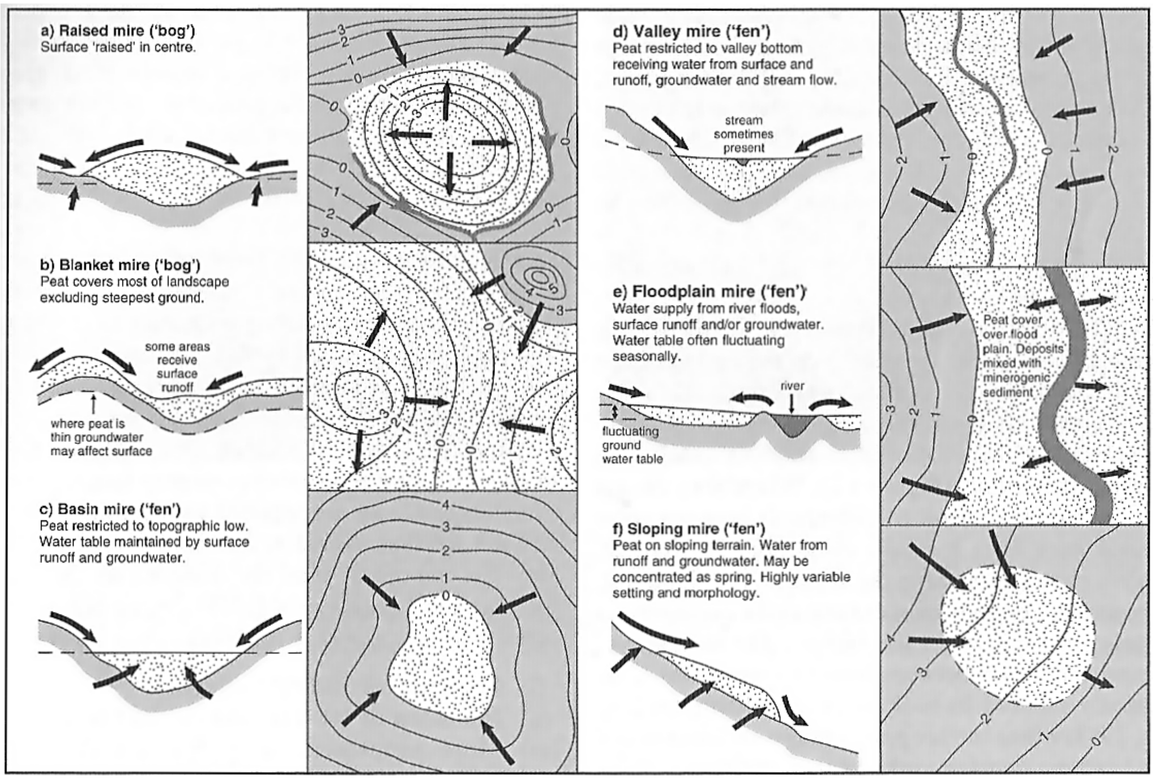


Figure 2.2.2. Hydromorphological classification of mires (from Charman, 2002).

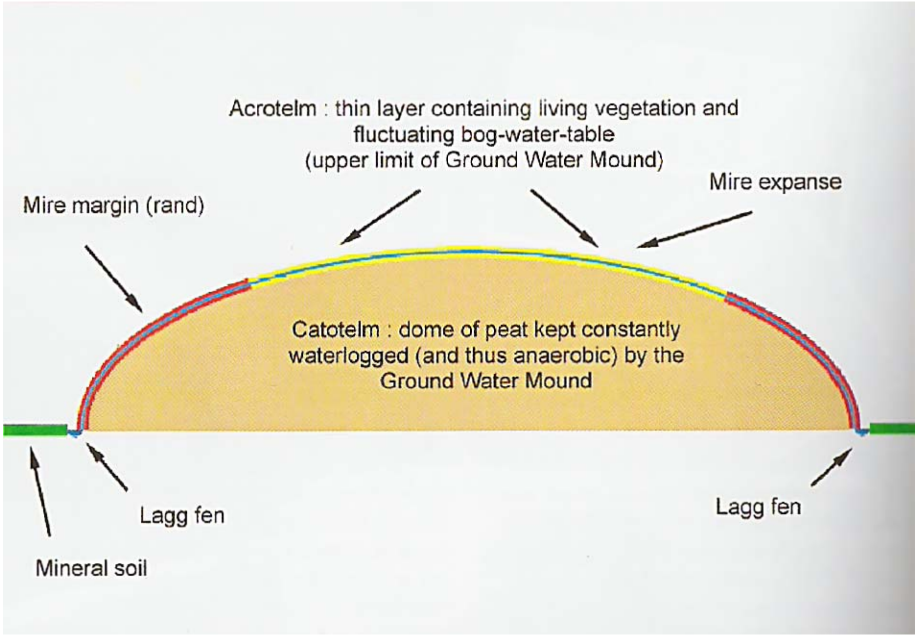


Figure 2.2.3. Cross-section of a raised-bog (from Lindsay, 2003).

Intermediate bogs, sometimes referred to as intermediate blanket-raised bogs (Charman, 2002) or ridge-raised bogs (Lindsay, 1995), occur where two raised bogs have grown together to form a single expanse of peatland and could perhaps be considered small mire complexes.

Blanket bogs essentially carpet the landscape over varied topography (Figure 2.2.2b). They perhaps ought to be considered as a mire complex since there may be some component raised bogs or minor minerotrophic elements, for example around springs and seepages (Charman, 2002). There is a wide range of peat thickness from deep peats of perhaps 6-7 m to shallower examples of 25-50 cm on steeper slopes (Charman, 2002). For peat to grow over steeper sloping terrain, extreme climatic conditions are required and most likely owe much of their formation to paludification (Lindsay, 2003). Suggested required conditions include minima of 1000 mm rainfall and 160 wet days (which by definition must account for at least 1 mm of precipitation) and a cool climate with small seasonal fluctuations in temperature (Immirzi *et al.*, 1992). The origins of the British blanket peats are thought to be intrinsically linked to prehistoric human activity, as decreases in evapotranspiration and increases in runoff following forest clearance produces increased soil moisture and raised water tables (Moore, 1975). Over 85% of peatland found within Britain (Table 2.2.3) is blanket mire (Lindsay, 1995).

Table 2.2.3 . Areas (ha) of different peatland types in Britain from Lindsay (1995).

Country	Fen	Raised bog	Blanket bog	Intermediate bog	Total
England	131 672	37 413	214 138	981	384 204
Scotland	1 215	27 892	1 056 798	10 653	1 095 958
Wales	2 867	4 086	158 770	85	165 808
Total	135 754	69 391	1 429 106	11 719	1 645 970

2.2.5. Peat decomposition (humification)

During decomposition dead plant matter undergoes a series of changes (Clymo, 1983):

- loss of organic matter, as gas or in solution as a result of leaching and attack by animals and micro-organisms
- loss of physical structure
- change of chemical state – e.g. production of new types of molecules

In the early stages of decay, polysaccharides are depolymerised by decomposers (Killops and Killops, 1993). Hemicellulose constituents are rapidly removed, followed by conversion of cellulose into glucose units. Lignin is more resistant, but a proportion is degraded, mostly under aerobic conditions, yielding large amounts of aromatic, phenolic and carboxylic acid (COOH) units. During these biochemical changes the main expelled products are gases, such as CH_4, NH_3, N_2O, N_2, H_2S and CO_2, together with H_2O (Killops and Killops, 1993). A large proportion of CO_2 is derived from the breakdown of carbohydrates, while lignin degradation is probably a significant contributor of CH_4. The products of peat decomposition are collectively referred to as humic substances.

2.3. Humic substances

2.3.1. Definition of humic substances

Humic substances are present in all waters but are most abundant in drainage from acid peats, forest litter deposits and sodic soils rich in organic matter (Hayes *et al*., 1989). Humic substances do not belong to a unique chemical category and cannot be defined in unique functional terms. Therefore operational definitions have been adopted (Table 2.3.1), though it is important to note that each fraction is a heterogeneous mixture of organic substances and not pure compounds.

Table 2.3.1. Operational definitions of humic substances (from Aiken *et al*., 1985).

Term	Definition
humic substances	a general category of naturally occurring, biogenic, heterogeneous organic substances from soil that can be characterised as being yellow to black in colour, of high molecular weight, and refractory
humic acid	a fraction of humic substances that is soluble at alkaline pH but precipitates at acidic pH
fulvic acid	a fraction of humic substances that is water soluble at alkaline and acidic pH
humin	a fraction of humic substances that is insoluble at any pH

Whilst these broad definitions are still considered to be valid, observations identifying the presence of lower molecular weight humic substances (e.g. Leenheer and Croué, 2003) are indicative of the ongoing enhancement of knowledge. Fulvic and humic acids have been most extensively studied (Malcolm, 1993), and therefore only these fractions are considered here in detail. There is general agreement that more extensive research is needed on other fractions.

2.3.2. Characteristics of humic substances

Humic acids have been found to be moderate in aliphatic character and high in aromatic content, while fulvic acids are high in aliphatic content and moderate in aromatic content (Malcolm 1993). Both fractions have high carboxyl and low methoxyl and phenolic content. In water draining from peatlands these are likely to arise from the degradation of lignin (Killops and Killops, 1993).

Humic acids and humin occur mostly in soils and sediments as part of the solid phase, while fulvic acids are more mobile and account for a major part of dissolved organic matter (DOM) in natural waters (Tipping, 2002). Clapp *et al*. (1993) suggest that the hydrogen bonding and van der Waals forces between the soluble fulvic and insoluble humic acids are insufficient to hold both types of macromolecules together. However, all drainage waters will contain some humic acids in solution (Clapp *et al*., 1993). The ratio of fulvic to humic acids ranges from approximately 10:1 in uncoloured waters to 3:1 in coloured waters (Malcolm 1993).

2.4. Dissolved organic carbon (DOC)

2.4.1. Definition of DOC

The presence of water-soluble humic substances in natural waters is visually apparent from the characteristic colours they impart (Aiken *et al.*, 1985), and often these waters are referred to as ‘humic waters’. While the depth of colour allows simple qualitative assessment of the concentration of natural organic matter (NOM), this is most comprehensively quantified in aquatic systems by the measurement of total organic carbon (TOC) (Leenheer and Croué, 2003). However, due to uncertainty in varying proportions of particulate matter in water samples, the dissolved organic carbon (DOC) parameter, synonymous with dissolved organic matter (DOM), was introduced in the 1970s (Malcolm, 1993) and is now the most widely used. Particulate organic carbon (POC) and DOC are arbitrarily divided by filtration through a 0.45 μm membrane, and are therefore purely operational definitions. POC is suggested to represent less than 10% of TOC (Leenheer and Croué, 2003).

Humic substances typically comprise about 50% of DOC (Tipping, 2002) but can account for as much as 65% in coloured waters (Malcolm, 1993). The remaining fractions of DOC may contain contribution from sources other than the breakdown of organic matter (Figure 2.3.1).

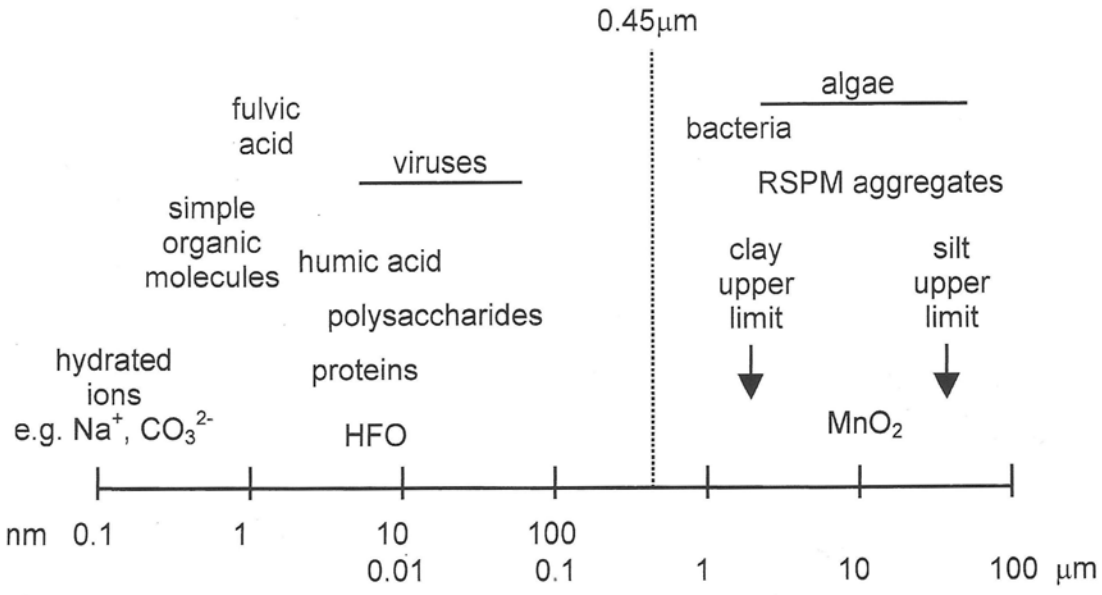


Figure 2.4.1. Chemical and biological components of natural waters indicating organics smaller than 0.45 μm that would be included in DOC (from Tipping, 2002).

2.4.2. Measurement of DOC

Combustion-infrared, wet-oxidation and persulphate-Ultraviolet (UV) oxidation (Clesceri *et al*., 1999) are accepted standard methods for DOC measurement. Direct measurement of DOC determined in this thesis will be performed using the persulphate-UV oxidation method, which is given in detail in Chapter 3.3.1.

While accepted methods for determining DOC provide reliable results, they are inherently time consuming, and consumables used in these processes, such as reagents, have associated costs. High-energy spectroscopic methods provide a quick alternative for the characterization of humic substances (Bloom and Leenheer, 1989), and may be appropriate for determination of DOC where this primarily derives from humic substances.

2.4.2.1. UV-visible Spectroscopy

Organic compounds in water absorb UV-visible radiation due to the presence of chromophores, such as aromatic carboxyl and phenolic groups (Bloom and Leenheer, 1989). Humic and fulvic acids absorb strongly in the UV region of the spectrum (200 – 400 nm), but above this region absorbance decreases with wavelength and the spectra have little structure (Figure 2.4.1). Water utilities measure water 'colour' using two common UV-visible spectroscopy methods, to determine UV-absorbance measured at a wavelength of 400 nm (au m^{-1}) or Hazen. Solutions of potassium chloroplatinate (K_2PtCl_6) tinted with cobalt chloride produce colours similar to natural waters. One degree Hazen (1 mg l^{-1} Pt/Co) is defined as the colour produced by 1 mg Pt l^{-1} (as K_2PtCl_6) in the presence of 2 mg l^{-1} Cobalt (II) chloride hexahydrate (Mitchell and McDonald, 1991/1992).

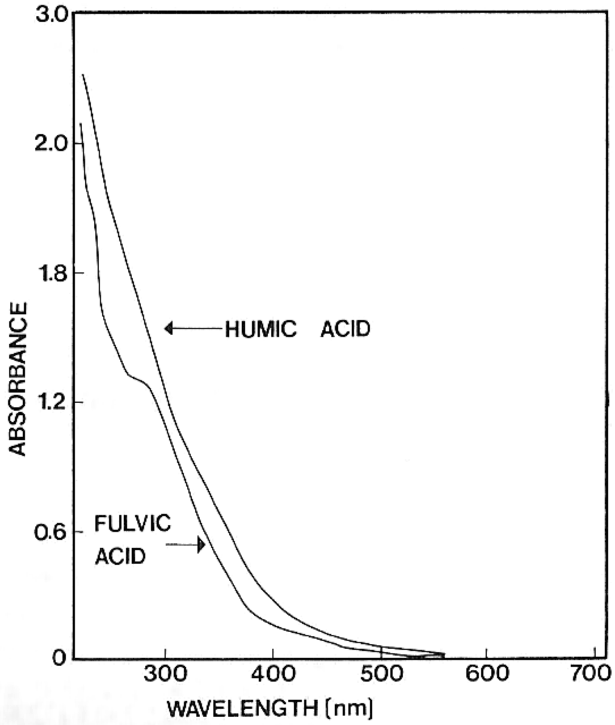


Figure 2.4.2. UV-visible absorption spectrum of a humic and fulvic acid (from Bloom and Leenheer, 1989)

2.4.2.2. SUVA

Most aquatic research limits UV spectroscopy to absorbance measured at a wavelength of 254 nm (Leenheer and Croué, 2003), which also allows calculation of a specific UV absorbance (SUVA) index, defined as UV absorbance measured at 254 nm (au m^{-1}) divided by DOC concentration (mg l^{-1}). SUVA can provide an indication of the molecular weight of natural organic matter (NOM) in water (Edzwald and Tobiason, 1999), thereby allowing inference of the chemical character. Aromatic groups tend to produce a higher SUVA index (Edzwald and Tobiason, 1999; Leenheer and Croué, 2003) and derive from the decomposition of more resistant plant material such as lignin (Killops and Killops, 1993). SUVA may therefore provide additional indication of the origin or age of DOC measured in drainage waters.

2.5. Significance of DOC

DOC is an important component of soil and aquatic environments and is involved in a number of geochemical processes, including pH buffering, nutrient cycling, ionic balance, mineral weathering, metal leaching and pollutant toxicity, mobility and bioavailability (Scott *et al*., 1998). DOC contributes to the global carbon cycle (Meybeck, 1993) and its export from peatlands represents a significant regional redistribution of terrestrial carbon (Pastor *et al*., 2003). DOC concentrations in freshwater streams, rivers and lakes vary from less than 0.5 mg dm^{-3} to 100 mg dm^{-3}, with highest values found for water draining peat catchments (Tipping, 2002).

In Britain, removal of aquatic DOC represents a major issue in water treatment (Naden and McDonald, 1989; McDonald *et al*., 1991; Watts *et al*., 2001) and has high operational costs associated. The current preferred method for removal of organic colour (DOC) utilises coagulation with metal additives (Sharp *et al*., 2006). Incomplete removal of colour results in water of low aesthetic quality and may also cause problems during disinfection processes, as humic substances react with chlorine to form potentially harmful disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Singer, 1999). Under current legislation in England and Wales the standard for colour is 20 mg l^{-1} Pt/Co and for THMs 100 ug l^{-1} (EU Drinking Water Directive 98/83/EC). Several water treatment works (WTWs) operated by Yorkshire Water Plc and United Utilities have recently experienced difficulty meeting THM limits in their finished drinking water (Goslan, 2003), and levels of DOC are also exceeding the design limit for treatment works.

2.6. Variability in DOC concentration

2.6.1. Seasonal variation

Seasonal variation in drainage DOC concentration from upland peat catchments is well documented (Naden and McDonald *et al*., 1989; McDonald *et al*., 1991; Mitchell and McDonald, 1992; Scott *et al*., 1998), with lower concentrations observed in summer months and higher concentrations in autumn or early winter. This has been attributed to enhanced decomposition of peat during drier periods and subsequent removal of DOC in periods of prolonged rainfall (e.g. Mitchell and McDonald, 1992).

2.6.2. Spatial variation

Spatial variability in DOC concentration has also been noted across upland catchments (e.g. Dawson *et al*., 2002; Monteith and Evans, 2005) and has been found to relate to stream discharge (Grieve, 1984), and physical catchment characteristics including catchment slope (Eckhardt and Moore, 1990; Aitkenhead *et al*., 1999; Andersson & Nyberg, 2008), altitude (Hope *et al*., 1997a; Clark *et al*., 2004) and cover of blanket peat (McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001).

2.6.3. Increasing trends

Increasing trends in DOC concentration have been observed in surface waters in Canada (Bouchard, 1997), northern and eastern USA (Stoddard *et al*., 2003), the Czech Republic (Hejzlar *et al*., 2003), Norway (Hongve *et al*., 2004), Finland (Vuorenmaa *et al*., 2006) and the UK (Freeman *et al*., 2001a; Worrall *et al*., 2004). Those observed in the UK, however, have been notably larger (Skeljkvale *et al*., 2005), with mean concentrations in rivers and lakes draining upland catchments increasing by 91% from 1988-2003 (Evans *et al*., 2005). Longer term data (e.g. Watts *et al*., 2001; Worrall *et al*., 2003b) suggest that these are part of a trend detectable since at least the 1970s and represent real increases in carbon loss rather than changes in discharge (e.g. Tranvik and Jansson, 2002), as both DOC concentration and flux have risen (e.g. Worrall *et al*., 2003b).

There has been considerable debate over the last decade regarding factors that might underlie the observed increases in DOC from peat soils. These include climatic change (e.g. Freeman *et al*., 2001a; Stoddard *et al*., 2003; Worrall *et al*., 2003b; Evans *et al*., 2005) and associated increases in enchytraied worm activity (Cole *et al*., 2002; Carrera *et al*., 2009), increasing atmospheric CO_2 (Freeman *et al*., 2004), hydrological change (Hongve *et al*., 2004; Evans *et al*., 2005), artificial drainage (Worrall *et al*., 2003b), severe drought events (Watts *et al*., 2001; Worrall and Burt, 2004), the removal of decomposition inhibiting phenolic compounds following prolonged water table drawdown (Freeman *et al*., 2001b), decreasing acid deposition (e.g. Stoddard *et al*., 2003; Evans *et al*., 2006; Vuorenmaa *et al*. 2006; Monteith *et al*., 2007) and increasing N deposition (e.g. Findlay 2005; Bragazza *et al*., 2006).

The widespread occurrence of increasing trends in DOC suggest that global and regional scale phenomena are important (Evans *et al*., 2008), yet they do not explain the markedly greater increase (Skjelkvåle *et al*., 2005) or the significant variation between adjacent blanket peat catchments observed in the UK (Yallop *et al*., 2008). For example, changes in sulphate and chloride deposition combined with a catchment acid sensitivity index could explain trends in DOC in north-eastern USA, Ontario/Quebec, Atlantic Canada, southern Nordic and northern Nordic regions, but not in the UK (Monteith *et al*., 2007). Additionally, out of 315 sites examined across the UK (Worrall *et al*., 2007), 18% have shown significant decreases in DOC concentration over the last 10 years, including a number of peat-dominated catchments. These observations suggest that more localised factors may be contributing to the UK increases (Worrall *et al*., 2003b; Evans *et al*., 2005).

2.6.4. Localised factors

2.6.4.1. Artificial drainage

Although drainage in the uplands can be traced to the eighteenth century, the activity began in earnest in the 1960s and 1970s (Holden *et al*., 2004). Moorland drains or ‘grips’ are ditches cut in rows on wet heath or blanket bog in an attempt to lower water tables and remove surface water, thus improving conditions for vegetation for grazing and game (Holden *et al*., 2004). Drainage activities are suggested to have ceased in 1995 when financial incentives were changed (Worrall *et al*., 2004a).

Stewart and Lance (1991) found that mean water tables near to drains in blanket bog were lower than in undrained bog, but that lowering was slight and confined to a zone only a few metres either side. The study suggests that the drains merely intercept surface run-off and only remove water from the peat along the edge, most likely due to low hydraulic conductivity at depth in blanket peat (Holden and Burt, 2003b). The effects of drainage are however suggested to be cumulative (Holden *et al*., 2006) and higher interstitial DOC concentrations have been found in drained peat catchments (Wallage *et al*., 2006). Although drainage has been suggested as an accentuating factor to changes in DOC over the last 30 years (Worrall *et al*., 2003b), Worrall *et al*. (2004a) note that changes in drainage over this period are not as extensive as the observed increases in DOC concentration, and highlight that some of the sites in the Acid Water Monitoring Network (AWMN) showing increases in DOC do not show any evidence of drainage.

2.6.4.2. Controlled burning

The application of burning as a management tool is suggested to date from as early as *c*.6000 BC in some areas of the English uplands (Caseldine, 1999). Fire was used primarily to improve grazing, and involved burning large areas of grassland and heath (Rackham, 1986). At some point, probably during the mid-1800s, the purpose of fire in the uplands changed to include the specific goal of managing habitat for red grouse *Lagopus lagopus scoticus* (Simmons, 2003).

The burning of heather in patches or narrow strips was advocated by Lovat (1911) and remains the current recommended practice outlined in the Heather and Grass Burning Code for England (Defra, 2007). The use of such burning techniques creates a mosaic of differing aged heather as is now distinct in contemporary aerial photography (see Chapter 3.2.2). It is not clear though how these practices have been adopted since the early 1900s, as quantitative information on burning in England is lacking prior to the 1970s. However, in the year 2000, 17% of heather-dominated moorland in the English uplands had been burned within the previous four years, equivalent to 114 km^2 burnt annually (Yallop *et al*., 2006a). Since 1970, the extent of new controlled burns has almost doubled from 15.1% to 29.7% (Yallop *et al*., 2006a), indicating intensification of this activity in some areas.

Much research on the dynamics of controlled burning and post-fire regrowth of vegetation was conducted in the 1980s (Hobbs and Gimingham 1980, 1984a, 1984b, 1987). Temperatures and fire intensity were found to increase with stand age, and following burning of very old stands of heather regrowth is extremely slow, often reliant upon seed germination (Hobbs and Gimingham, 1984a). This leaves ground bare for many years after the fire and, compared to unburnt moor, prone to more variable and extreme temperatures (Fullen, 1983; McDonald *et al*., 1991), erosion (Imeson, 1971; Yeloff *et al*., 2006), freeze-thaw processes (Maltby, 1990) and higher wind speeds (Fullen 1983; McDonald *et al*., 1991).

However, very little is known about the effects of burning on moorland hydrology, sediment release and water quality (Holden *et al*., 2007; Ramchunder *et al*., 2009). Some studies (e.g. Ward *et al*., 2007; Clay *et al*., 2009) suggest that burning has no effect on interstitial or surface water DOC concentration, while Worrall *et al*. (2007) found interstitial DOC to be lower. Conversely, Yallop *et al*. (2008) found a highly significant relationship between the amount of burning on areas of deep peat and water colour in drainage waters.

Although the studies discussed above have provided valuable insight to the spatial and temporal variation in DOC concentration from upland peat catchments, the potential role of land management as a controlling factor has not been fully explored.

Chapter 3: General methods

3.1. Introduction

This chapter describes the methods used in aerial image processing and land cover classification relevant to Chapters 5-8 in this thesis and provides assessment of the errors associated with these techniques. Detailed methods of water sample analysis undertaken in Chapter 5, processing of water utility colour data used in Chapter 7 and commonly used statistical tests are also provided in this chapter.

3.2. Aerial imagery

3.2.1. Image processing

To allow accurate estimation of the areal extent of features of interest from remotely sensed data, imagery must first be geometrically corrected (Rocchini, 2004). Three image correction techniques are commonly adopted for aerial imagery (Novak, 1992): polynomial, projective and differential rectification (orthocorrection). Polynomial and projective methods provide relatively quick but only approximate correction as they do not use elevation information and therefore cannot account for any relief displacement. For images covering areas with little variation in topography, polynomial and projective correction provide acceptable results (Rocchini and Di Rita, 2005). However, over varied topography polynomial and projective correction can lead to errors in estimation of feature area of up to 100% (Rocchini, 2004). Due to the topography of the upland areas examined in this thesis, correction for relief displacement was key to providing accurate land use area estimations. All aerial imagery used to assess land use in Chapters 5-8 (Table 3.2.1) was therefore orthocorrected prior to interpretation.

Table 3.2.1. Year, source, format and resolution of imagery used in this thesis.

Image year	Source	Format	Resolution (cm)
1966/68	RAF/National Monuments Record	B/W	25
1976	Ordnance Survey / Countryside Commission	B/W	50
1989	Countryside Commission / Peak District NPA	RGB	50
1990	National Monuments Record	B/W	25
1993	National Monuments Record	RGB	25
1995	Cambridge University	RGB	25
1999 *	Getmapping Plc	RGB	25
2001 *	GeoPerspectives™	RGB	25
2003	GeoPerspectives™	RGB	25
2005	Cambridge University / Cranfield University	RGB	25

* Imagery supplied as orthocorrected product

The process of orthocorrection uses a series of collinearity equations (Leica Geosystems, 2003) to define the relationship between the camera, the image and the ground. Each variable associated with the relationship is defined with respect to a coordinate space and coordinate system. Camera calibration certification allows the image coordinate system (x, y) to be determined from the location of a series of fiducial marks on imagery. In the absence of calibration detail, image pixel coordinates can be used to represent the image coordinate system. The image space coordinate system, which defines the position of the image coordinates inside the camera, is identical to the image coordinate system, except that it adds a third axis (z; Figure 3.2.1). The ground coordinate system is defined as a three-dimensional coordinate system using a known map projection. For the imagery used in this research, the ground coordinate system was defined as the Ordnance Survey British National Grid (OSGB36), so X, Y and Z coordinates were measured in metres.

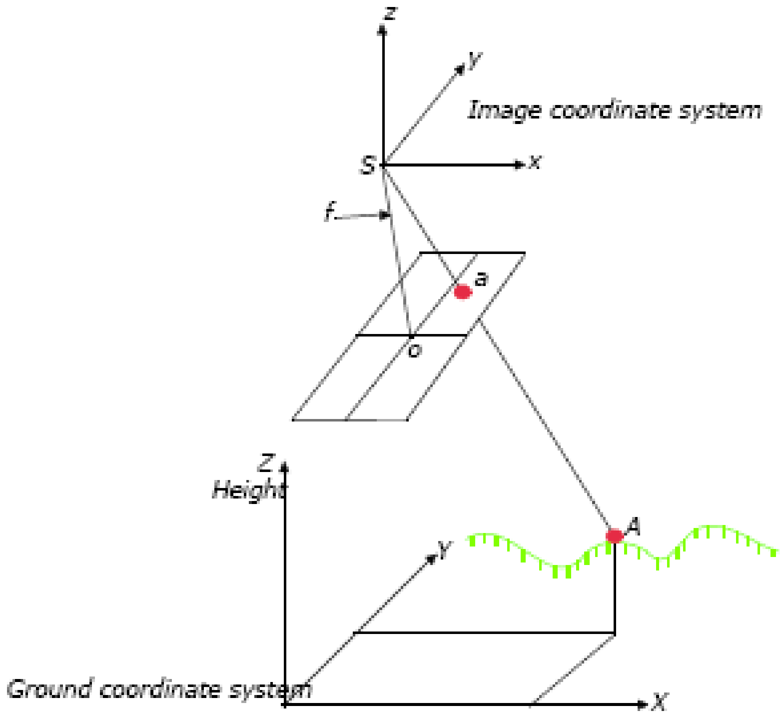


Figure 3.2.1. Image space and ground space coordinate system (Leica Geosystems, 2003).

To establish the relationship between the image, the camera and the ground, a number of ground control points (GCPs) are required. GCPs are features on the ground for which an accurate location is known in all three dimensions (X, Y, Z). For the imagery corrected in this research, GCPs were identified and the locations obtained from Ordnance Survey (OS) Land-Line® 1:10 000 data (X, Y) and OS Panorama 1:50 000 digital terrain models (DTMs) (Z). Accuracies for Land-Line® 1:10 000 and Panorama 1:50 000 data are reported to be ±4.1 m and ±5 m respectively (Ordnance Survey, 2006).

Triangulation is the process whereby the mathematical relationship between the image, the camera model and the ground is defined, during which the error or residual of each GCP is calculated and expressed as a root mean square error (RMSE). In an iterative process, GCPs with large errors can be adjusted if the error is due to data input or discarded if the error arises from another source such as the map or DTM, and triangulation performed again. The theoretical minimum number of GCPs required to establish the relationship between image space and ground space is three per image (Leica Geosystems, 2003). To improve the quality of orthocorrection, nine GCPs, distributed as evenly as possible, were identified for each image. Prominent and historically consistent features including buildings and structures around reservoirs, farm outbuildings, OS triangulation points, walls and field boundaries were preferred features for GCP collection. The reliability of these features as GCPs was established during the triangulation process and those causing large errors were discarded. The RMSE of triangulation was kept below 1.0, which equates to an accuracy of better than one pixel (25 cm or 50 cm). A number of tie points, which identify the same feature in different images but have no geographical information defined, were added to further improve the quality of image correction where adjacent images were corrected as a block of images.

To assist the consistent interpretation of land cover in catchments covered by more than one image, for each year of capture, adjacent orthophotographs were merged into single images (mosaics). During the mosaic process, differences in tonal and spectral response between images were equalised as best possible. All image processing was undertaken using ERDAS Imagine 8.7.

3.2.2. Aerial photographic interpretation (API)

Six land cover classes defined by major vegetation groups were consistently identifiable across all imagery used in this research:

- unimproved grassland;
- semi-improved grassland;
- coniferous plantation;
- broadleaf woodland;
- ericaceous dominated (predominantly *Calluna*) moorland;
- grass/sedge dominated moorland.

Controlled burning of *Calluna* dominated communities in the British uplands is a prominent feature in contemporary aerial photography, as new and recent burns appear visually distinct from darker background vegetation owing to their characteristic bright signature (Figure 3.2.2). However, identification and classification of burned and unburned areas is not straightforward. Yallop *et al.* (2005) note that almost all large blocks of *Calluna* within background vegetation will likely have been burned at some point, as a prime driver for such management is to increase the dominance and condition of *Calluna* for red grouse. Therefore any classification scheme for burning needs to consider the regeneration of vegetation following burning to judge the time elapsed since a burn occurred.

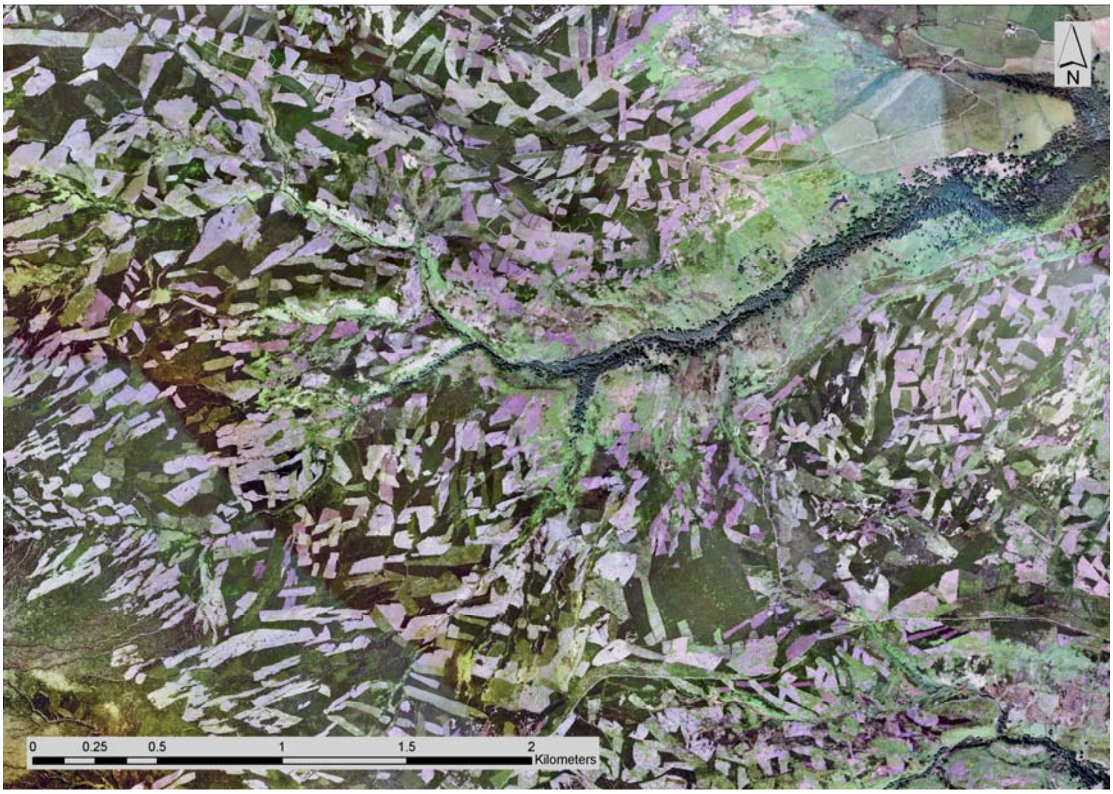


Figure 3.2.2. New and recent controlled vegetation burning visible in aerial photography as bright objects compared to background moorland vegetation (image covers an area of moorland in the Peak District captured in 2005).

Yallop *et al.* (2005) found that four classes of vegetation regrowth following burning (predominantly related to *Calluna*) can be identified in aerial imagery. These were defined as:

- Class 1, new burn 'scar' with no visible regrowth of dwarf shrub/*Calluna*;
- Class 2, recent burn with only partial canopy of regenerating dwarf shrub/*Calluna*;
- Class 3, a visually smooth, dark and relatively complete dwarf shrub/*Calluna* canopy within a burn scar;
- Class 4, no visible remains of burn scar, visibly pale with 'lumpy' texture of degenerating *Calluna* canopy.

While Classes 1–3 represent vegetation where evidence of burning is still visible, Class 4 represents areas that have not been burnt for a considerable period (Figure 3.2.3).

Figure 3.2.3. Appearance of API burn classes in aerial photography.

Classification of burns into the four API classes has been shown to be highly consistent, with Yallop *et al*. (2006a) reporting overall areal concordance between interpreters of 94%. Although the actual age or time since burn that each class represents varies according to the speed of *Calluna* regeneration, Yallop *et al*. (2006a) suggest possible use of Gimingham's (1959) post-fire growth phases to interpret the classes in relation to age of *Calluna* regrowth (Figure 3.2.4). Further assessment of what these classes represent on the ground is examined in Chapter 4.

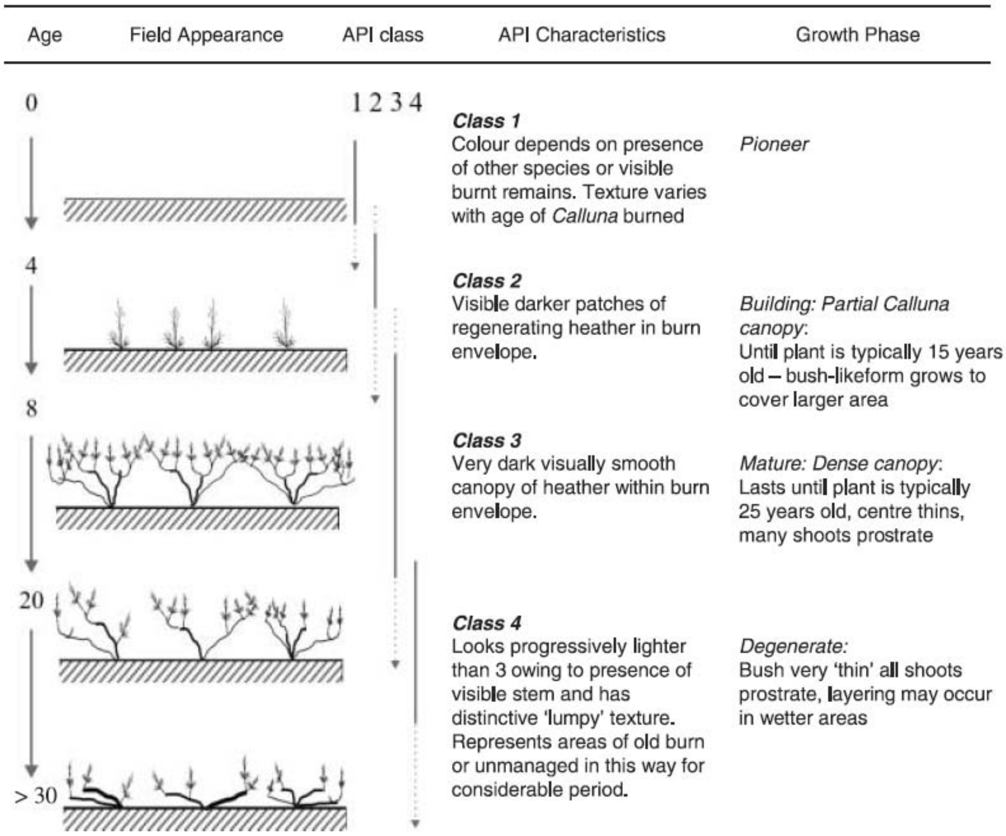


Figure 3.2.4. Illustrative relationship between API of growth following burning in *Calluna vulgaris* within the growth phase contexts of Gimingham (1959) (from Yallop *et al*., 2006a).

3.2.3. Estimation of class area

Traditionally, estimation of the area of features in aerial imagery has been derived from hand-drawn polygons on acetate sheets laid over contact prints (e.g. Ward *et al*., 1972). Today this is more widely performed using Geographical Information Systems (GIS) to digitise polygons (Jenson, 2000). This process is, however, slow and laborious, particularly in decisions over the placement of digitised boundaries. An alternative approach, which uses an image sampling technique developed for use in ArcGIS (Clutterbuck, 2004; Clutterbuck and Yallop, 2005) has been shown to reduce the time for area estimation by at least 75% compared to digitising techniques, whilst maintaining an estimated area compliance of more than 94%. This method has been used to provide estimates of the extent of vegetation burning from an area greater than 1000 km^2 in the North Pennines (Yallop *et al*., 2006b).

The sampling approach uses a grid of points positioned over the area of interest within an image. The image is interpreted by eye and each point within the grid assigned an API class either individually or in bulk where a number of points fall within a large area covered by a single land cover class. The technique removes some of the problems associated with digitisation where a boundary between two land cover classes is not distinct. For example, where there is a transition from *Calluna* dominated moorland to grass/sedge moorland, a sample point is simply assigned the major vegetation type at that location. Following guidelines outlined by Clutterbuck (2004), sample grids with spacings of 25 m and 35 m between points were used to map land use for catchments smaller or greater than 3 km^2 respectively in Chapters 5-8.

Determination of the error associated with digitisation is problematic, requiring repeated digitisation of areas of imagery. The error of an area estimate derived from point sampling of aerial imagery can however be determined from the regression model of the 'known' area of features within an image against the area estimated using this method. Areas of API Classes 1-4 were digitised in the area of moorland in Broomhead catchment (20 km^2) for the years 1968, 1976, 1989, 1995, 1999, 2001, 2003 and 2005 (see Chapter 7). Each digitised polygon was assumed to be an example feature and therefore its area a known value with which a point sample estimation could be compared. The total area of each class was calculated for each year providing 32 accurately known areas. A sample grid with 35 m spacing was created within ArcGIS and intersected with the polygon layers and each point assigned the class of the polygon it fell in.

Broomhead catchment also contains eight of the small headwater catchments (<3 km^2) examined in Chapter 5. The areas of Classes 1-4 within these eight smaller catchments were calculated for each year, and these were then sampled with a 25 m sample grid.

3.2.4. Accuracy of area estimation using point sample tool

For catchments greater than 3 km^2 sampled using a 35 m spaced grid, the standard error in area estimation was ±1.42 ha (Figure 3.2.5).

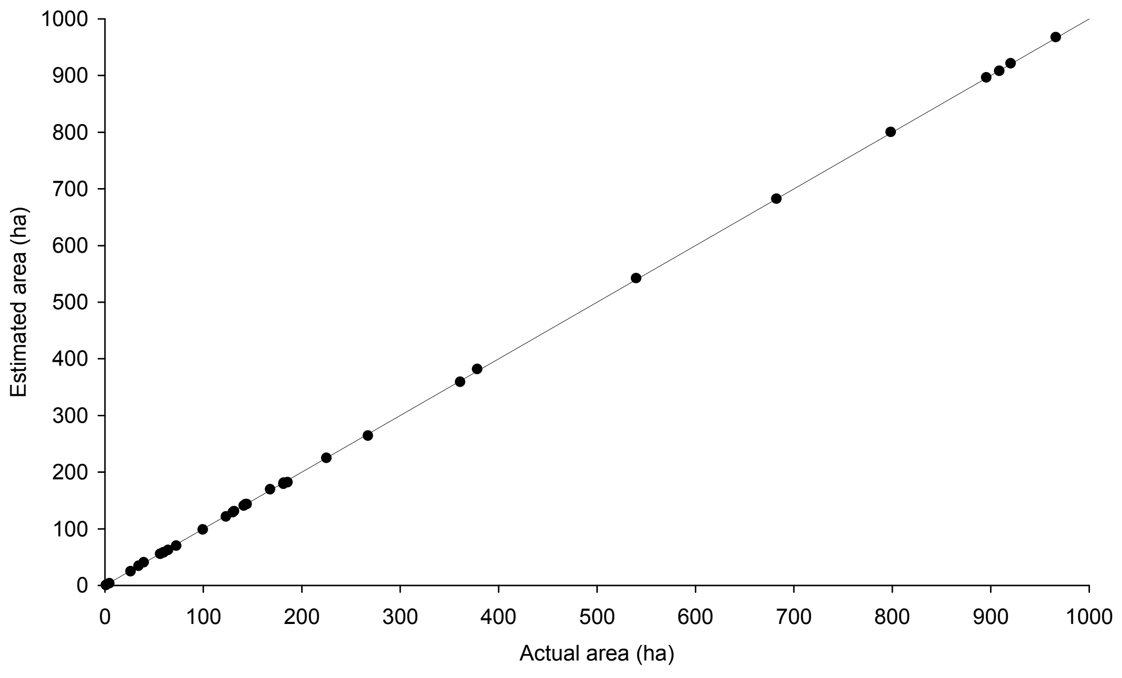


Figure 3.2.5. Actual area of feature in image against area estimated using 35 m image point sample grid for catchments larger than 3 km^2 (1:1 line shown).

For catchments smaller than 3 km^2 sampled using a 25 m spaced grid, the standard error in area estimation was ±0.48 ha (Figure 3.2.6).

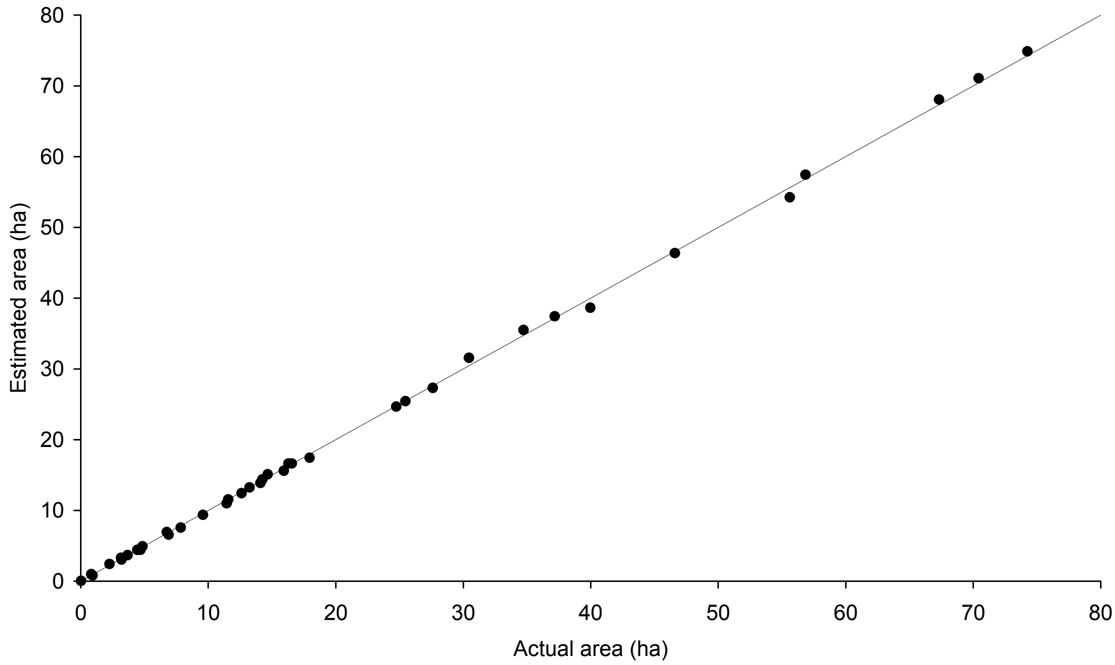


Figure 3.2.6. Actual area of feature in image against area estimated using 25 m image point sample grid for catchments smaller than 3 km^2 (1:1 line shown).

3.3. Determination of DOC concentration and water colour

3.3.1. Sample analysis

Prior to analysis, all samples collected from the headwater catchments examined in Chapter 5 were filtered through Whatman 0.45 µm filter membranes and were stored in the dark at 4°C. DOC concentration was measured using a Burkard Scientific Series 2000 Segmented Flow Analyser with a detection range of 1-50 mg C l^{-1}. Samples were first acidified and sparged (flushed) with oxygen to remove inorganic carbon as carbon dioxide. Samples were then run through a Burkard Scientific Analyser in duplicate, where each sample was mixed with acidified potassium persulphate and irradiated with ultraviolet (UV) light to convert organic carbon to carbon dioxide. As the carbon dioxide permeates through a gas diffusion membrane into a buffered phenolphthalein solution, a change in colour occurs, which was detected using a colorimeter at 550 nm. DOC concentration was then determined from a six-point calibration curve of DOC:colour.

Water colour was determined as Hazen measured at a wavelength of 455 nm and UV absorbance measured at 254 nm. Hazen was measured using a HACH DR/2000 spectrophotometer, where one Hazen unit is calibrated to equal 1 mg l^{-1} platinum as chloroplatinate ion. Absorbance was measured as absorbance units per centimetre (au cm^{-1}) using a Nicolet Evolution 100 spectrophotometer.

3.3.2. Accuracy of DOC measurement

The six-point calibration curve of DOC:colour was determined prior to analysis using five standard solutions containing 10, 20, 30, 40 and 50 mg C l^{-1}. A Burkard Scientific Analyser measures DOC for five groups of ten samples in any one ‘run’. Between each group of samples a standard solution was measured to check and adjust for drift in measurement. In addition to this ‘self-test’ error check, ten samples of each standard solution were measured as ‘unknowns’ to further assess measurement error.

Mean concentrations determined for each standard were not significantly different from the true concentration as identified by a t-test (Table 3.3.1).

Table 3.3.1. DOC concentration measured using a Burkard Scientific Analyser for standard solutions used for measurement calibration.

Standard DOC ($mg\ l^{-1}$)	Mean measured DOC ($mg\ l^{-1}$)	Standard error	t(10)	*p*
10	9.15	0.41	-2.09	0.07
20	20.13	0.18	0.73	0.48
30	29.02	0.57	-1.73	0.12
40	39.78	0.49	-0.45	0.66
50	50.04	1.26	0.03	0.98

3.3.3. Accuracy of water colour (Hazen and UV absorbance)

The HACH and Nicolet Evolution spectrophotometers were maintained within the suggested service and calibration intervals. With no opportunity to test the absolute accuracy of colour measurements, the consistency of repeat measurement was determined on a range of water samples collected in December 2005. Each sample was measured ten times using both methods.

Repeat measurements of absorbance (Tables 3.3.2) and Hazen (Table 3.3.3) were found to be highly consistent, with minimal or no variation from the mean.

Table 3.3.2. Repeat measurement of UV absorbance at 254 nm ($au\ m^{-1}$) for December samples.

Sample	N	Minimum	Maximum	Mean	Std. Deviation
1	10	17.3	17.4	17.39	0.03
2	10	29.5	29.5	29.50	0
3	10	41.7	41.7	41.70	0
4	10	72.7	72.7	72.70	0
5	10	117.7	117.8	117.73	0.05
6	10	168.1	168.3	168.24	0.07
7	10	191.6	191.7	191.62	0.04

Table 3.3.3. Repeat measurement of Hazen for December samples.

Sample	N	Minimum	Maximum	Mean	Std. Deviation
1	10	26	26	26.0	0
2	10	49	50	49.8	0.42
3	10	93	94	93.7	0.48
4	10	185	187	185.9	0.57
5	10	361	362	361.1	0.32
6	10	498	500	498.3	0.68

3.4. Short-term variation in DOC concentration

Seasonal variation of drainage DOC concentration is well documented (Mitchell and McDonald, 1992; Scott *et al*., 1998), yet shorter term variation on a daily or even hourly basis is not so well understood. Owing to the number and location of catchments examined in Chapter 5, catchment drainage for all 50 catchments was sampled over a five-day period. Short-term variation in drainage DOC concentration over this period was assessed for the stream draining one of the catchments located on Keighley Moor. This stream was selected primarily for ease of access, but the location also offered security for unattended sampling equipment. Using a Bűhler Montec xian 1000 automatic sampler, stream water was sampled every four hours over a 92 hour period (24 samples).

DOC concentration determined for stream water sampled over the 92 hour period showed strong consistency (Figure 3.4.1) with only one sample measurement more than two standard deviations from the mean (4.86 mg C l^{-1}). This indicates that short-term variation in DOC concentration is minimal and should not significantly affect the interpretation of results derived from catchments sampled over a five-day period.

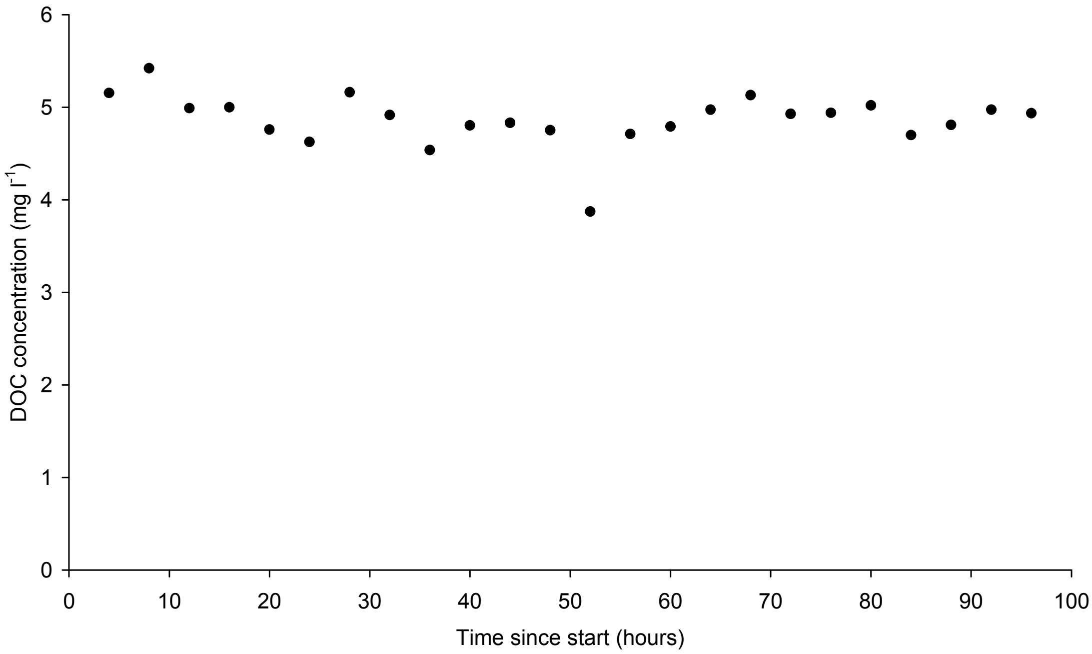


Figure 3.4.1. DOC concentration of water sampled over a 92 hour period at Keighley Moor in March 2006 (mean concentration = 4.86 mg C l^{-1}, standard deviation = 0.29).

3.5. Water utility colour data

3.5.1. Derivation of consistent time series in Hazen

In Chapter 7, DOC concentrations for five reservoir catchments were estimated from water colour (Hazen) measured at respective water treatment works (WTW). For Lower Laithe and Keighley Moor catchments, the complete water colour record available was measured as Hazen. However, for Agden, Broomhead and Langsett catchments, colour was determined as absorbance units measured at 400 nm for the period March 1979 to December 1989 (Table 3.5.1). To estimate DOC concentrations for this period, colour measured as absorbance was first converted to Hazen following the method in Watts *et al*. (2001). Mean monthly colour in absorbance units was calculated for the period March 1979 to December 1989 and was subsequently converted to Hazen using the relationship between Hazen and absorbance (Equation. 3.5.1; Watts *et al*., 2001) determined for water sampled from Broomhead WTW.

Table 3.5.1. Water colour data availability for catchments examined in Chapter 7.

Reservoir	1961 – 1979 *	1974 – 1978	1978 – 1989	1990 - 2006
Agden	Hazen	Hazen	Absorbance	Hazen
Broomhead	Hazen	Hazen	Absorbance	Hazen
Langsett	Hazen	Hazen	Absorbance	Hazen
Lower Laithe	n/a	n/a	n/a	Hazen
Keighley Moor	n/a	n/a	n/a	Hazen

* annual mean Hazen presented in McDonald *et al*. (1991); n/a not available

$$\text{Hazen} = 11.77 * \text{absorbance} \pm 35.61 \tag{3.5.1}$$

3.5.2. Correction for particulate organic carbon (POC)

Prior to 1984 all absorbance measurements were determined on unfiltered waters (termed apparent colour) and therefore include contribution from particulate organic matter/carbon (POC). Although POC has been found to account for less than 8% of TOC in drainage from low relief catchments (Billet *et al*., 2004), sediment input to some upland reservoirs in the southern Pennines has been shown to be greater than national averages (Labadz *et al*., 1995). The particulate content of the water from the study catchments creates visible artefacts within the historical record, as early measurements of Hazen derived from apparent absorbance appear anomalously high (Figures 3.5.1-3.5.3). Apparent absorbance measurements prior to 1984 were therefore 'adjusted' using the conversion factor derived by Watts *et al*. (2001) to compensate for particulate matter in water sampled from Broomhead (Equation 3.5.2).

$$A_T = 1.06 + 0.63 * A_A \pm 1.50 \tag{3.5.1}$$

where A_T is true colour (au m^{-1}), A_A is apparent colour (au m^{-1}) and a 95% confidence interval is given.

3.5.3. Potential uncertainty in estimated DOC

Adjusted colour data (true colour) for Agden, Broomhead and Langsett for the period 1979-1984 appear consistent with the 1979 annual mean Hazen presented in McDonald *et al*. (1991) and with colour data from 1985 (Figures 3.5.4-3.5.6). However, it must be recognised that the particulate content of water in samples will vary unpredictably, and it is therefore not possible to determine the absolute uncertainty in DOC concentrations estimated for this period. In addition, it is not clear whether colour measured as Hazen prior to 1980 was determined for filtered samples (Watts *et al*., 2001), although the concordance between the early 1980s colour data adjusted for POC and the annual mean values for 1979 suggests that samples may have been filtered, at least in the 1970s.

Despite the potential uncertainty, early colour data provide a valuable indication of historical change in colour and DOC. Therefore the analysis presented in Chapter 7 was performed over two time periods (1990-2005 and 1966/8-2005) to allow discrimination of any potential artefacts within the early data. No correction was applied to data recorded prior to 1980.

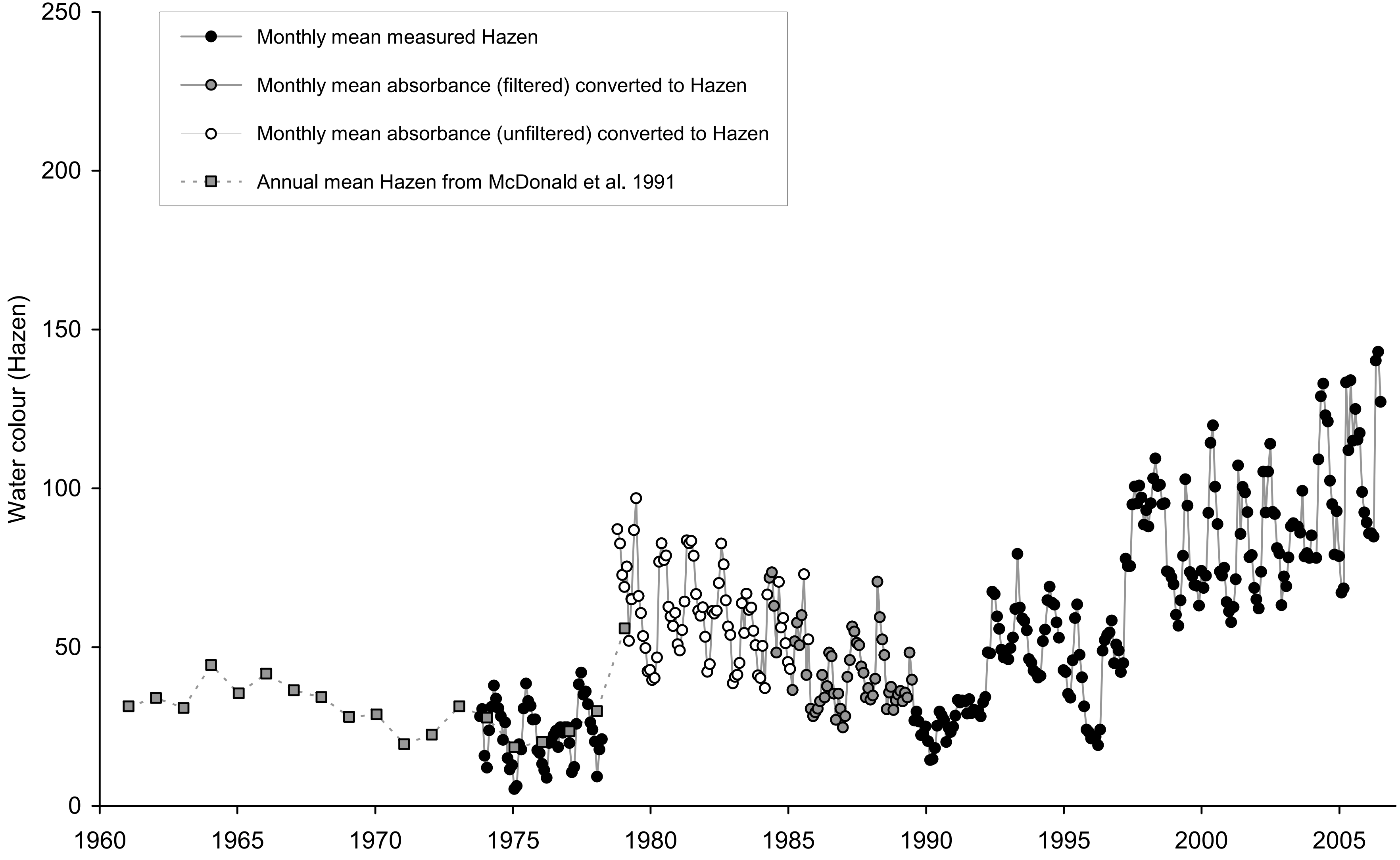


Figure 3.5.1. Time-series of water colour in Hazen sampled at Agden WTW.

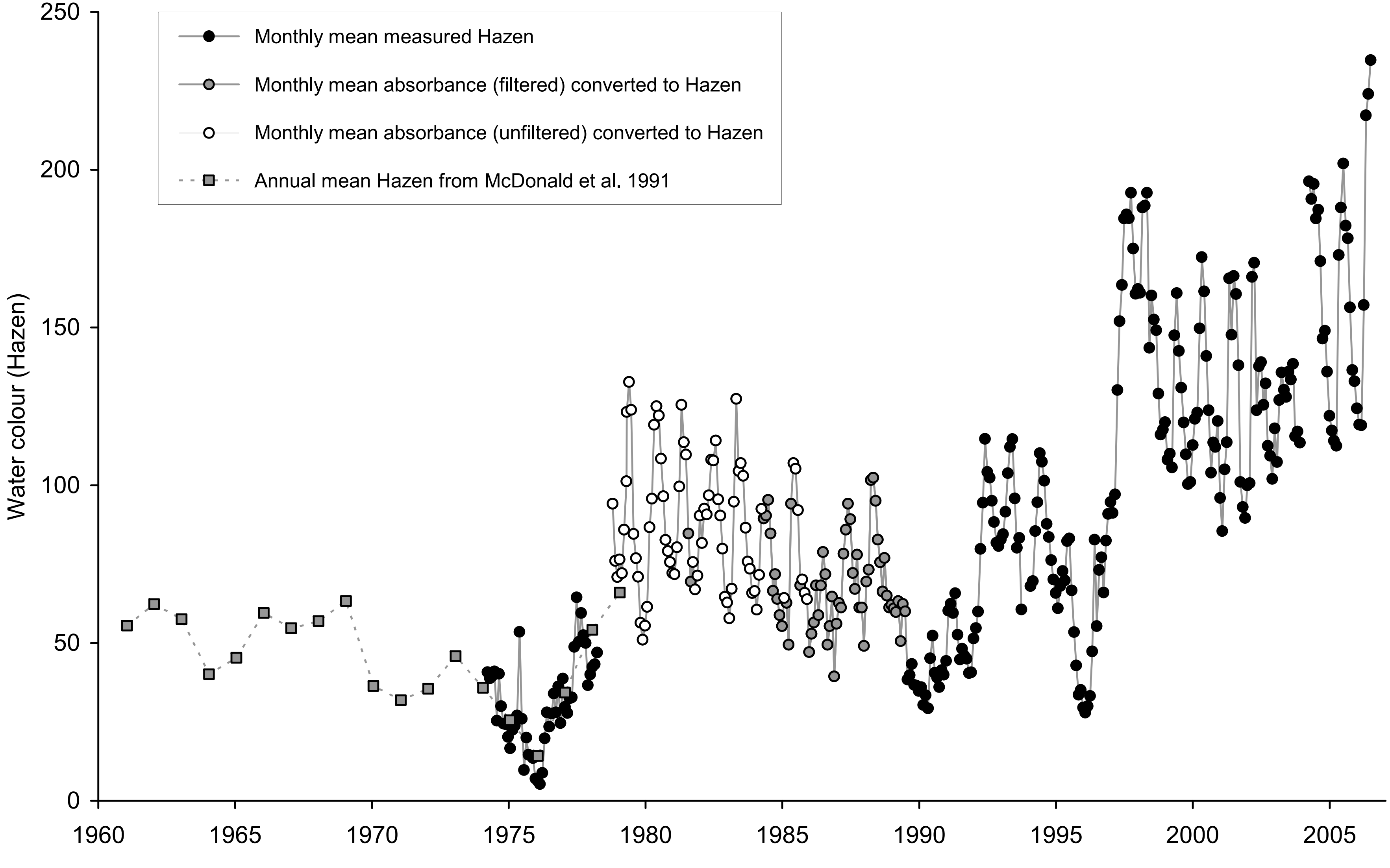


Figure 3.5.2. Time-series of water colour in Hazen sampled at Broomhead WTW.

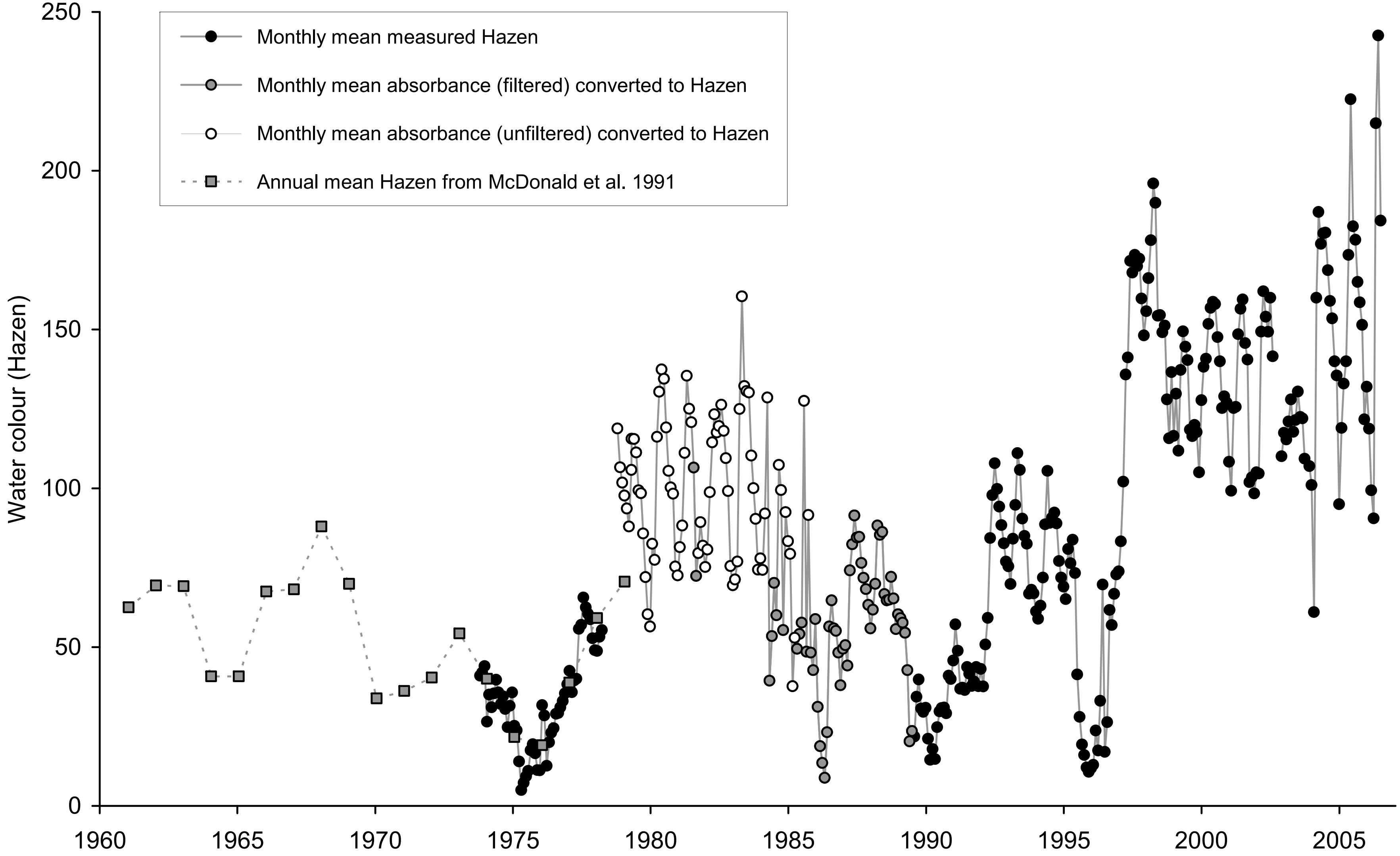


Figure 3.5.3. Time-series of water colour in Hazen sampled at Langsett WTW.

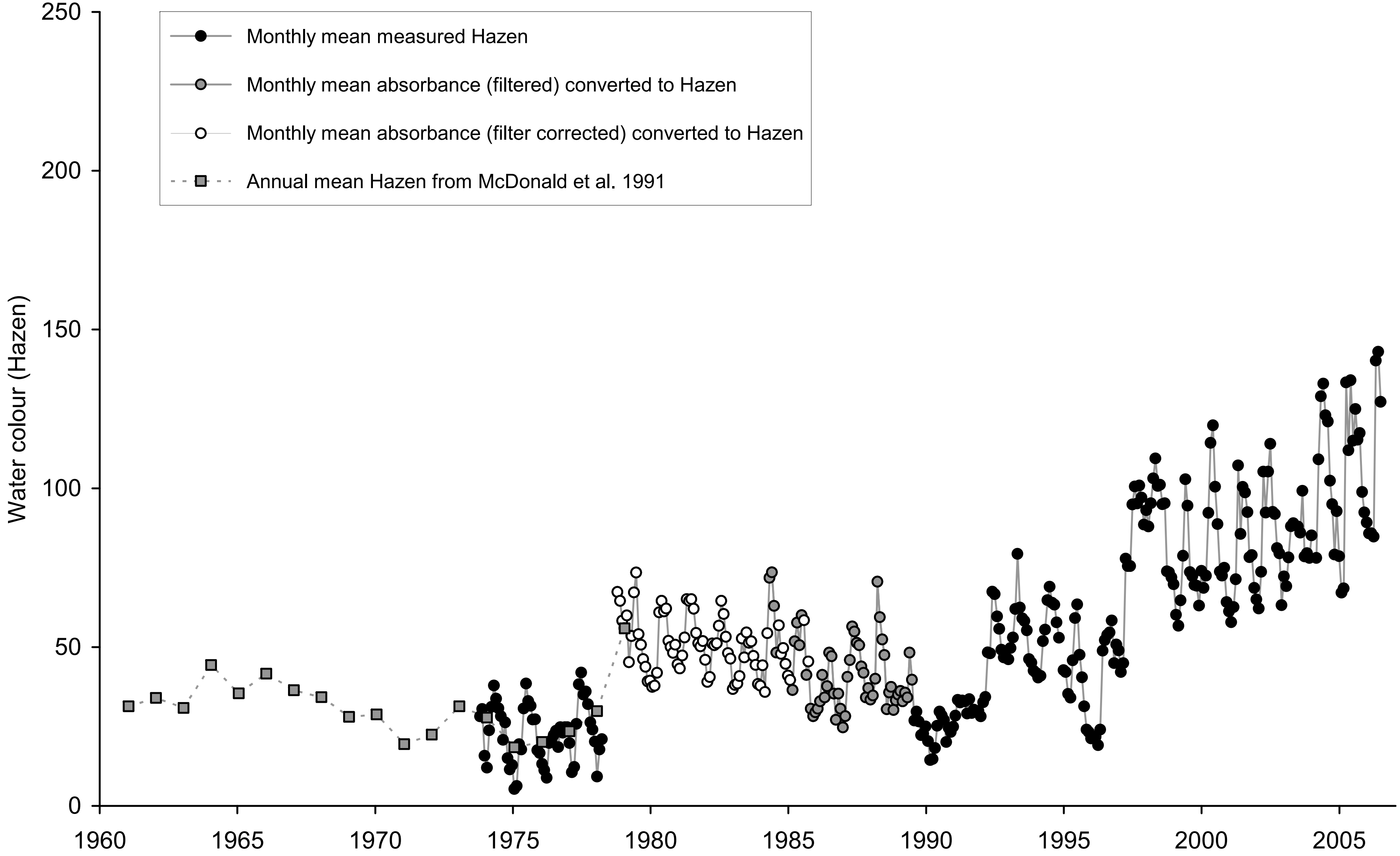


Figure 3.5.4. Time-series of water colour in Hazen sampled at Agden WTW, corrected for POC.

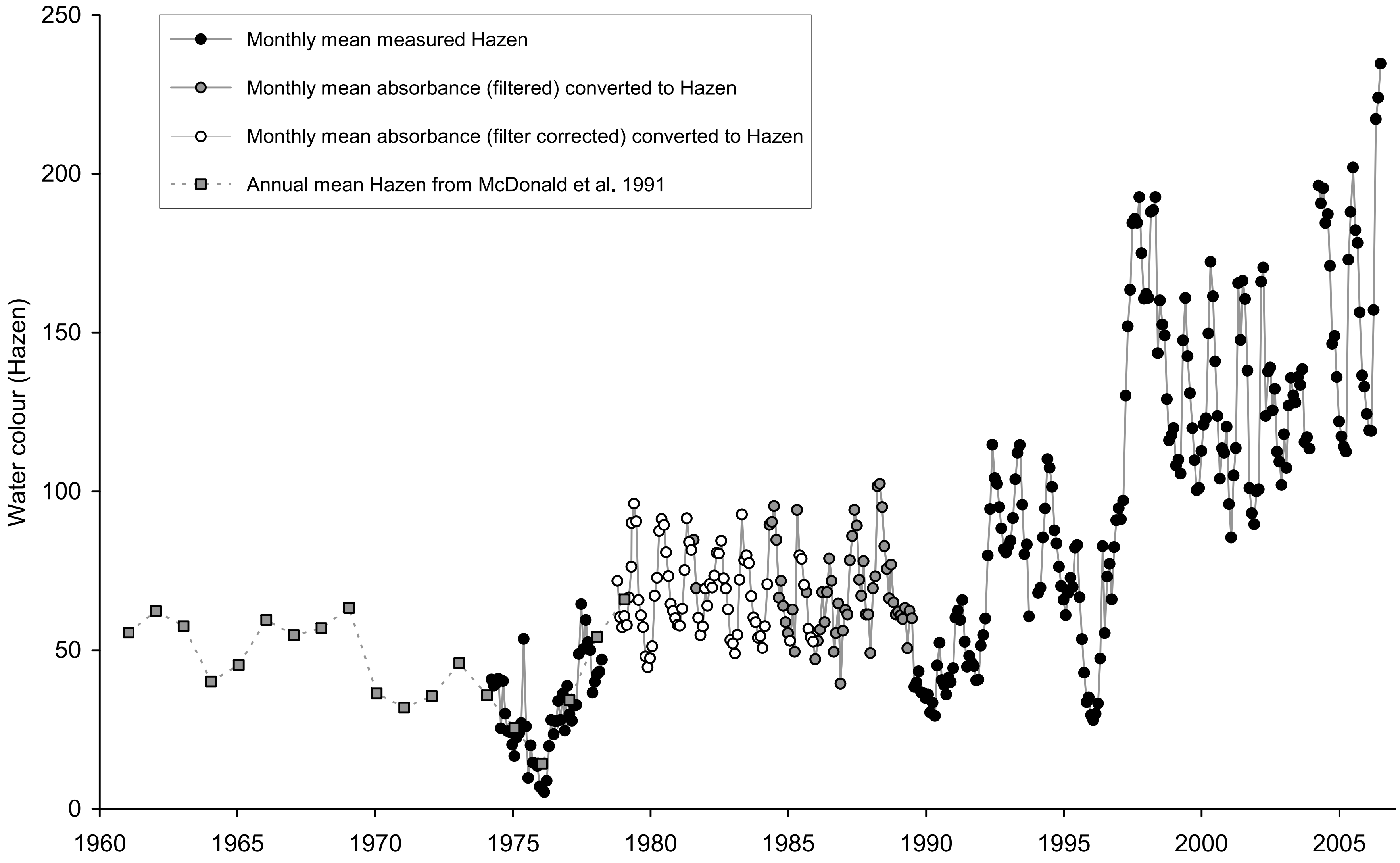


Figure 3.5.5. Time-series of water colour in Hazen sampled at Broomhead WTW, corrected for POC.

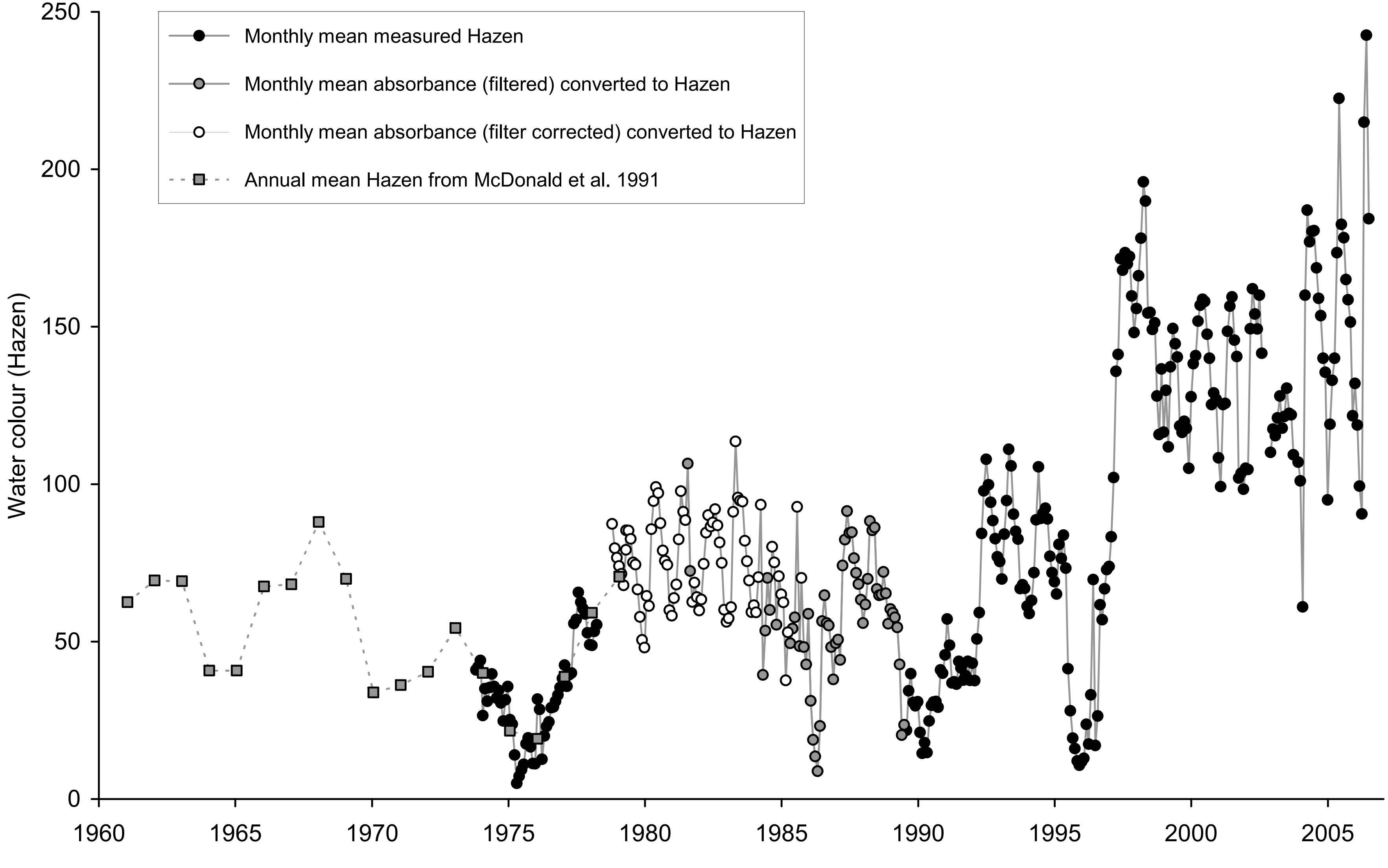


Figure 3.5.6. Time-series of water colour in Hazen sampled at Langsett WTW, corrected for POC.

3.6. Statistical methods

3.6.1. Arcsine square-root transformation

The distribution of proportion data is truncated by both tails as all values must lie on a scale with absolute limits of 0 and 1. Errors which might arise in analysis are greatest if the observations are grouped at one end of the scale. The appropriate transformation for proportion data is the arcsine square-root transformation (Fowler and Cohen, 1990: Equation 3.6.1).

$$\sin^{-1}\sqrt{x} \tag{3.6.1}$$

3.6.2. Seasonal Kendall Test

The Seasonal Kendall Test (SKT) was proposed by Hirsch *et al*. (1982) for the detection of trends in monthly water quality data. SKT is a non-parametric test that is robust with respect to seasonality in time series, missing or tied data, and does not depend on the data being normally distributed (Hirsch *et al*., 1982). To perform the test, the Mann-Kendall statistic S, and variance Var(S) are first calculated for each month over all years of data availability (Equations 3.6.2 and 3.6.3).

$$S_i = \sum_{k=1}^{n_i-1} \sum_{j=k+1}^{n_i} \operatorname{sgn}\left(x_{ij} - x_{ik}\right) \tag{3.6.2}$$

where j>k, n_i is the number of data (over years) for month i, and

$$\begin{aligned} \operatorname{sgn}(x_{ij} - x_{ik}) &= 1 \qquad \text{if } x_j - x_k > 0 \\ &= 0 \qquad \text{if } x_j - x_k = 0 \\ &= -1 \qquad \text{if } x_j - x_k < 0 \end{aligned}$$

$$Var\left(S_i\right) = \frac{1}{18}\left[n_i\left(n_i - 1\right)\left(2n_i + 5\right)\right] \tag{3.6.3}$$

Equation 3.6.3 shown here is simplified as no tied data were present in the data analysed using this test in this research. The full formula can be found in Hirsch *et al*. (1982).

The seasonal statistics S_i and Var(S_i) are then summed (Equations 3.6.4 and 3.6.5) and a Z statistic calculated (Equation 3.6.6). The sign of Z indicates whether the trend is upward or downward, and Z is referenced in normal distribution tables to test for significance.

$$S' = \sum_{i=1}^{12} S_i \tag{3.6.4}$$

$$Var(S') = \sum_{i=1}^{12} Var(S_i) \tag{3.6.5}$$

$$\begin{aligned} Z &= \frac{(S_i - 1)}{[Var(S')]^{1/2}} && \text{if } S' > 0 \\ &= 0 && \text{if } S' = 0 \\ &= \frac{(S_i + 1)}{[Var(S')]^{1/2}} && \text{if } S' < 0 \end{aligned} \tag{3.6.6}$$

The magnitude of a trend is estimated as the median of between-year differences in values (Q) for all months, where the value for individual months is calculated using Equation 3.6.7.

$$Q_i = \frac{x_{ij} - x_{ik}}{j - k} \tag{3.6.7}$$

where $j<k$

3.6.3. Inverse distance weighting interpolation

The simplest form of inverse distance weighting was proposed by Shepard (1968). The interpolated value for a point is calculated as the average of the values of the closest surrounding points, weighted by the inverse of the distance to those points (Equation 3.6.8).

$$F(x,y)=\sum_{i=1}^{n} w_i f_i \tag{3.6.8}$$

where n is the number of points used to interpolate the value, f_i are the values at the known points and w_i are the weight functions assigned to each point. The weight function is given in Equation 3.6.9.

$$w_i = \frac{h_i^{-p}}{\sum_{j=1}^{n} h_j^{-p}} \tag{3.6.9}$$

where p is the power parameter (commonly p=2), and h_i is the distance from the interpolated point to the point of known value.

Chapter 4: Characteristics of land management classes (specifically controlled burning)

4.1. Introduction

The assessment of land use and management over large spatial extents, such as the catchments that will be examined in Chapters 6 and 7 (up to 22 km^2), precludes comprehensive field survey and requires a remote sensing approach such as aerial photographic interpretation (API). Land use is commonly defined by dominant vegetation types visible in aerial photography (e.g. Taylor *et al*., 2000; see Chapter 3.2.2), but determination of land management is not so straightforward. In the UK uplands, livestock grazing and controlled burning for red grouse game shooting are currently the most extensive forms of land management undertaken (Simmons, 2003). Assessment of grazing requires knowledge of stocking densities and repeat monitoring of vegetation in the field (Hulme *et al*., 1999). Burning management, however, has previously been assessed from aerial photography (Hester and Sydes, 1992; Yallop *et al*., 2006a; 2006b).

Current guidance for management of *Calluna*-dominated environments for red grouse recommends rotational burning of narrow strips up to 30 m in width (Defra, 2007), to create a mosaic of differing aged stands of *Calluna*. These burn patches can be classified into four API burn classes defined by their visual appearance in aerial imagery (Chapter 3.2.2), and this approach was adopted to estimate the extent of burn management in Chapters 5 to 7. Classification of burns into these API classes has been shown to be highly consistent, with Yallop *et al*. (2006a) reporting overall areal concordance between interpreters of 94%. However, what these classes represent on the ground, and how burning might change the vegetative environment, is less well defined. The aim of the study presented in this chapter is to examine the characteristics of burn Classes 1-3 (where evidence of burning is still visible) to determine the vegetative cover of each class and typical rates of regrowth. The objectives defined to undertake this were:

i. select areas of moorland burned in the past 10-15 years;
ii. select burns of Classes 1-3 to include a continuum of age of burn for analysis;
iii. establish species composition, height and density of sward in selected burns in field survey;
iv. determine characteristics of each class and typical regrowth rates.

4.2. Methods

4.2.1. Selection of moorland and burn scars

Areas of moorland for potential field survey were initially stratified to four study areas in the South Pennines and North Yorkshire Moors that will be examined in Chapter 5. This selection was subsequently restricted to areas of blanket peat moorland located in eight reservoir catchments (Table 4.2.1) for which permission to conduct extensive vegetation survey was obtained from landowners. To provide a continuum of ages of burn scar for analysis, burn scars visible as API Classes 1-3 were identified within these areas of moorland from year 2005 aerial photography using ArcGIS. A total of 250 burn scars were selected for potential field survey, comprising between 80-85 burns of each class. The geographical coordinate of the centroid of each burn was derived in ArcGIS to assist navigation to the burns in the field using GPS equipment. As no evidence of burning is visible in Class 4, areas of moorland in this background class were not assessed.

Table 4.2.1. Location of blanket peat moorland (by reservoir catchment) and number of burn scars by API Class examined in field survey.

Catchment	Class 1	Class 2	Class 3
Broomhead	20	30	4
Fewston	6	11	0
Keighley Moor	6	6	0
Langsett	18	10	3
Lower Laithe	4	0	0
Midhope	6	8	7
Snailsden	7	1	1
Thruscross	13	18	2

4.2.2. Field survey

Burns visited were sampled using 1 m^2 quadrats. The number of quadrats assessed per burn was determined by the size of the burn with a general aim to collect a minimum of ten quadrats per burn. The location of each quadrat was recorded using Trimble® GeoXT™ handheld GPS units. In each burn visited, all vascular plants were identified to species level and recorded as a visual estimate of percentage cover restricted to 5% divisions. Major and distinctive bryophytes (e.g. *Sphagnum spp.*) were also recorded to species and the rest categorised into pleurocarpous or acrocarpous moss groups. The amount of bare surface (exposed peat) and *Calluna* height were also recorded. In total 1662 quadrats were assessed in summer 2005, comprising 181 burns (Table 4.2.1).

4.2.3. Determination of stand age

Using historical aerial imagery captured in 2005, 2003, 2001, 2000, 1999 and 1995, the year in which each burn scar appeared was used to establish its age. As imagery was captured in the summer months and controlled burning is undertaken from October to April (Defra, 2007), ages were determined at 0.5 year intervals from summer 2005. Dating of burn season was possible for 119 of the 181 available burn scars. For the remaining 62 burn scars the possible range of ages was refined using the height of *Calluna* measured in the field and the relationship between the *Calluna* height and age determined for the 119 exactly dated burns. For each burn, the mean measured height of *Calluna* was divided by the slope of the *Calluna* height-age regression to produce an age prediction. The predicted age was rounded up to the previous burn season to account for late recovery of *Calluna* from seed germination (Hobbs and Gimingham, 1984b), unless the rounded up age fell outside of the known possible age range (i.e. had not appeared in an image dated for that year), in which case predicted age was taken as the nearest known possible age.

4.2.4. Regeneration of vegetation and rate of canopy closure

The mean cover of each species and bare ground were calculated from quadrat data for each burn scar. These data were then averaged by age of burn to derive mean cover of species and bare ground for each growth season. Regeneration of vegetation and the rate of canopy closure were defined as the rate of increase of vascular plant cover in burns. This was assessed by plotting the age of burn against mean cover of vascular plants. The rate of *Calluna* regeneration and persistence of exposed peat surface were also assessed by plotting age of burn against both these variables.

4.2.5. Characteristics of burn Classes 1 to 3

Mean cover of vascular plants, *Calluna* and exposed peat were calculated for burns classified as Classes 1-3. The difference between vascular plant cover and exposed peat represents 'opportunistic' bryophyte cover which was frequently found detached from the peat (Figure 4.2.1). These bryophytes may not provide a protective layer over a peat surface and a second assessment of exposed peat was therefore calculated as all non-vascular plant cover.

Figure 4.2.1. Example of 'opportunistic' bryophyte cover in burn patch visibly detached from peat surface.

The duration of Class 1 and 2 burns as visible in aerial imagery was assessed from 'survivorship' curves (Yallop *et al*., 2006a) which were produced for each class by plotting the proportion of burns still classified in these classes against growth season. As Class 4 was not assessed, duration of Class 3 burns could not be estimated.

4.3. Results

4.3.1. Species composition

A total of 34 vascular plant species were recorded in the burn patches. The most frequently recorded plant was heather (*Calluna vulgaris*), which was present in 1593 quadrats (95.7%). Other frequently occurring species included bilberry (*Vaccinium myrtillus*) and hare's tail and common cotton grasses (*Eriophorum vaginatum* and *E. angustifolium*) (Table 4.3.1). *Sphagnum spp*. were recorded in only 75 quadrats (5%).

Table 4.3.1. Vascular plant species most frequently recorded in field survey.

Species	Common name	Occurrences	%
Calluna vulgaris	Heather	1593	95.7
Eriophorum vaginatum	Hare's tail cotton grass	771	46.3
Vaccinium myrtillus	Bilberry	673	40.4
E. angustifolium	Common cotton grass	498	29.9
Deschampsia flexuosa	Wavy hair-grass	462	27.7
Empetrum nigrum	Crowberry	177	10.6
Dryopteris dilatata	Broad buckler fern	83	5.0
Rumex acetosella	Sheeps' sorrel	63	3.8
Juncus effusus	Soft rush	43	2.6
J. squarrosus	Heath rush	40	2.4

4.3.2. Age of burns

The 119 exactly dated burns ranged in age from 0.5 years (burned the previous season) to 6.5 years. The *Calluna* height-age regression indicates that the average rate of growth of *Calluna* for the burns examined is 3.7±3.1 cm yr^{-1} (Figure 4.3.1). With age interpolation, 62 further burns were dated to a maximum age of 11.5 years.

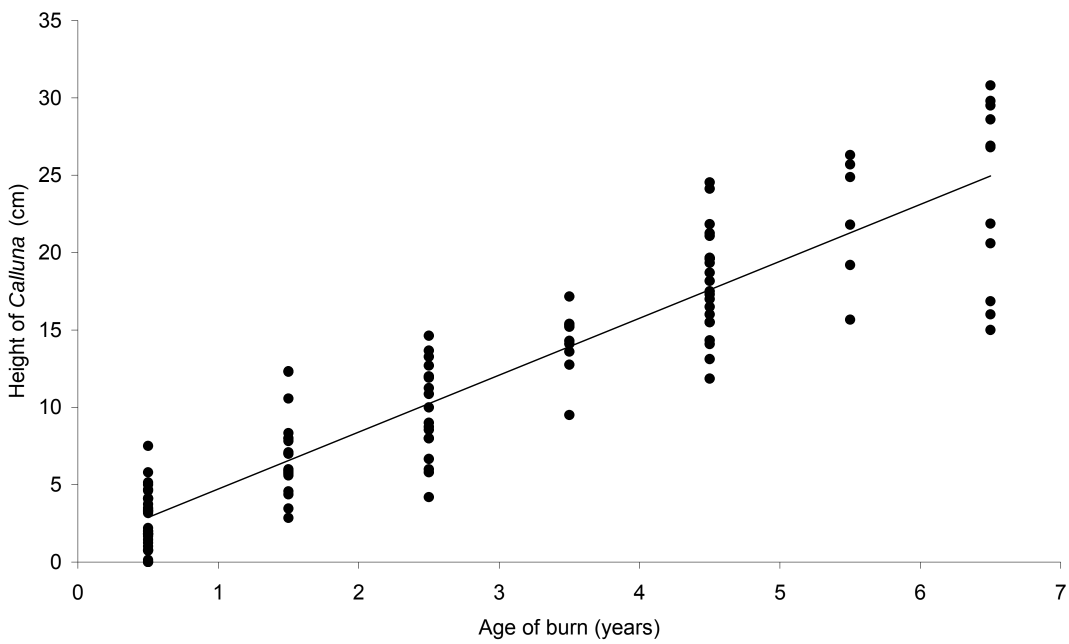


Figure 4.3.1. Burn age against height of *Calluna* for 119 exactly dated burns (each point represents the mean measured height in an individual burn; slope = 3.7 cm yr^{-1}).

4.3.3. Regeneration of vegetation and rate of canopy closure

Percent cover of both vascular plants and *Calluna* increased linearly with age of burn for the 119 exactly dated burn patches (Figures 4.3.2 and 4.3.3). Owing to the uncertainty in extrapolating beyond this age range (a non-linear age-cover relationship will occur at some point after 6.5 years), the rate of increase in cover (canopy closure) was determined from regression of burn age against percent cover for burns up to 6.5 years old (vascular plants 13.5% yr^{-1}; *Calluna* 12.3% yr^{-1}). Taking 80% cover to indicate burn 'recovery' (100% cover may not always be achieved), on average vascular plant recovery occurs 6.2 years after a burn event, with *Calluna* recovering at 6.8 years.

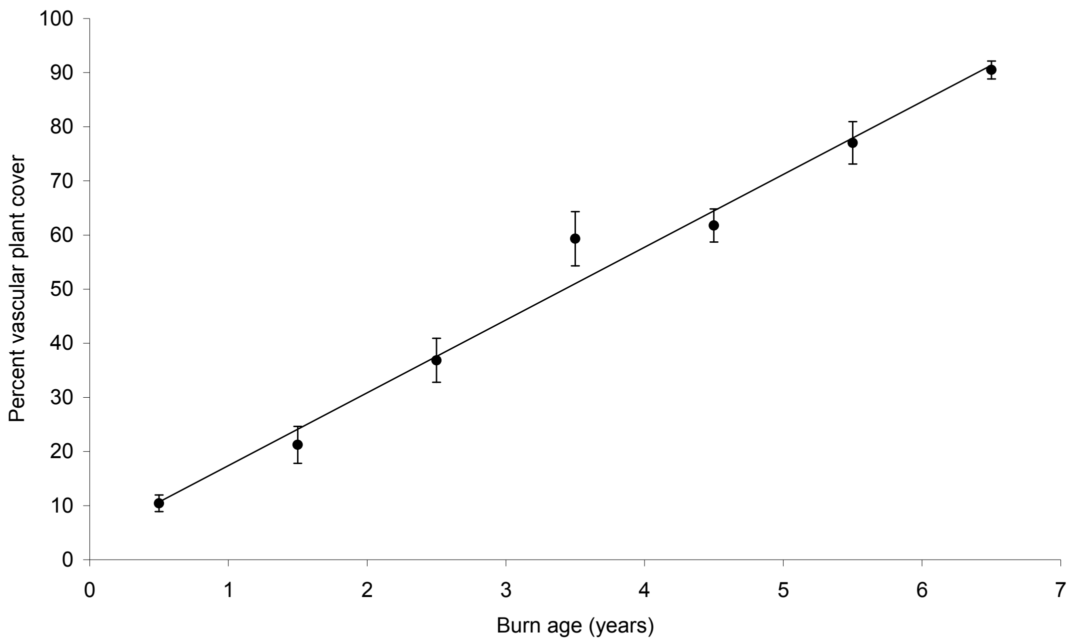


Figure 4.3.2. Burn age against percent vascular plant cover for 119 burns examined in the field (rate of increase in cover = 13.5% yr^{-1}; error bars show standard error).

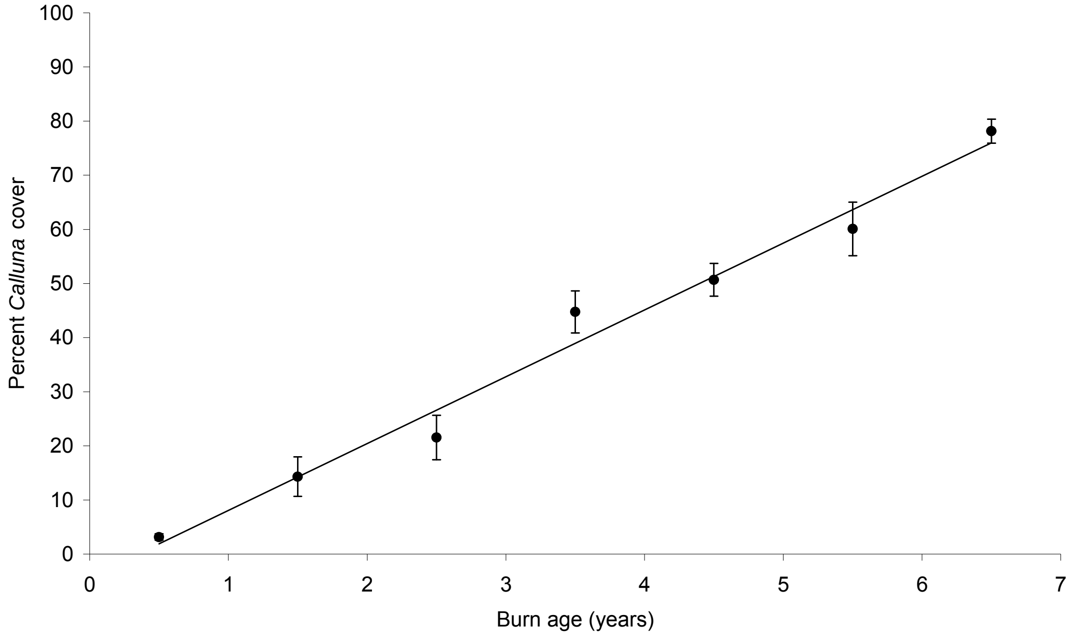


Figure 4.3.3. Burn age against percent *Calluna* cover for 119 burns examined in the field (rate of increase in cover = 12.3% yr^{-1}; error bars show standard error).

Percent bare ground (exposed peat surface) appears to show a non-linear, exponential decrease with burn age (Figure 4.3.4).

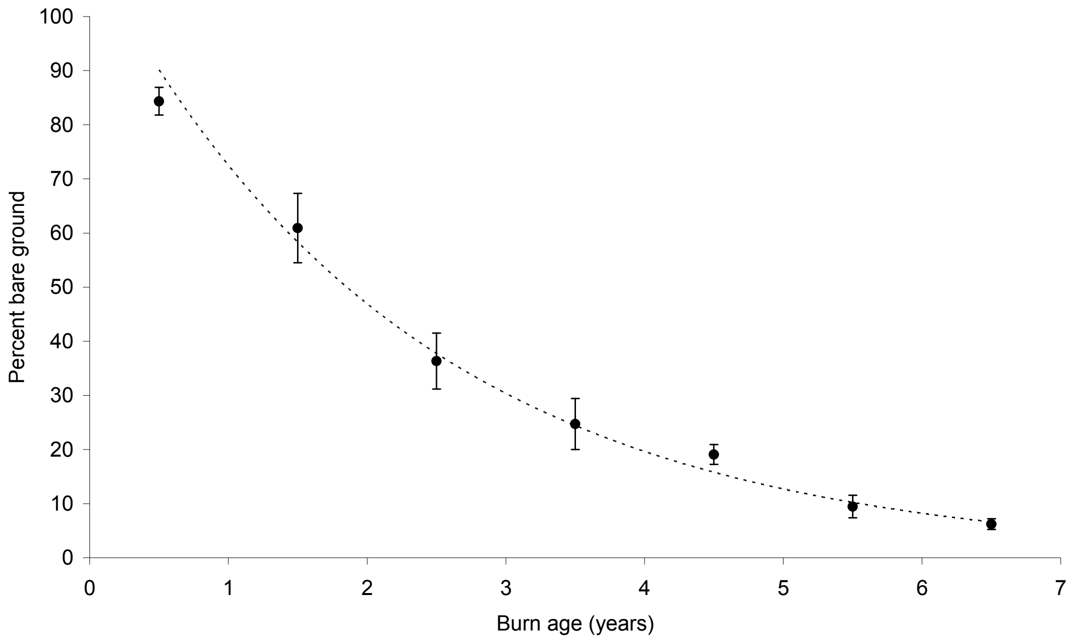


Figure 4.3.4. Burn age against percent bare ground for 119 burns examined in the field (error bars show standard error; exponential curve fitted).

Despite the linear increase in both vascular plant and *Calluna* cover determined for burns up to 6.5 years old, recovery in some areas was found to be slower than this general trend. For example in Fewston catchment, a burn estimated to be 9.5 years old was found to have vascular plant cover of only 50%, with 20% exposed peat surface. While this could appear to be an error of burn dating, an adjacent burn estimated to be 5.5 years old was found to have vascular plant cover of 11%, with 41% exposed peat surface. Both of these burns were visible in year 2000 imagery (Figure 4.3.5) and therefore occurred no later than the burning season October 1999 to April 2000 (i.e. at least 5.5 years before field survey). Of particular note, less than 300 m away from these two slow recovering burn patches, the remains of pine stumps typically dated at >4000 years BP (Simmons, 2003) have been re-exposed (Figure 4.3.6), indicating a loss of perhaps several metres of blanket peat.

Observations in Broomhead catchment indicates that controlled burning may cause disturbance to subsurface layers within peat, as well as expose the peat surface (Figure 4.3.7).

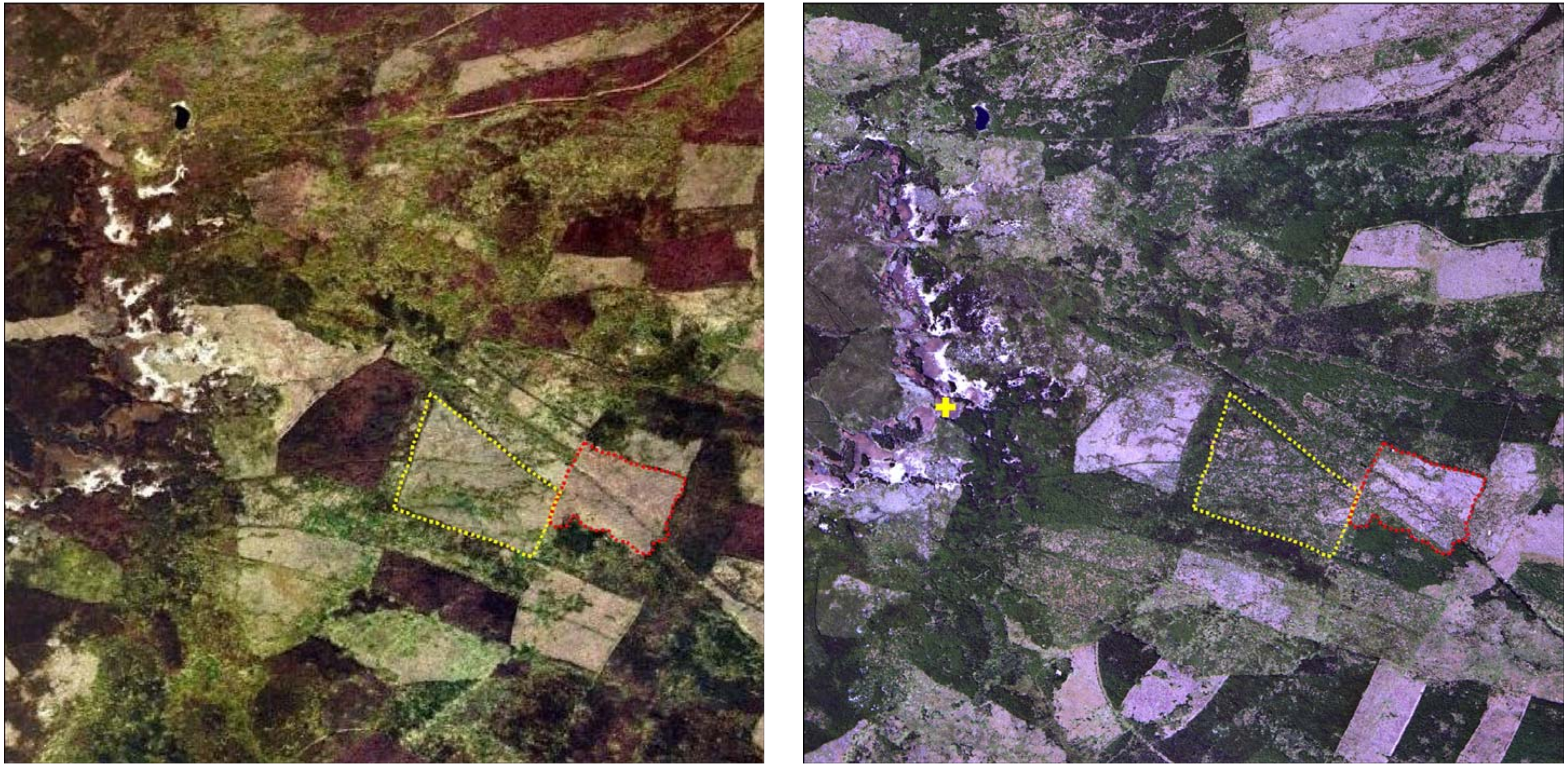


Image captured in summer 2000 | Image captured in summer 2005

Figure 4.3.5. Recovery of two controlled burns in Fewston catchment as visible from aerial photography between the years 2000 and 2005. Year 2005 field survey found 20% bare ground in burn highlighted in yellow (dated 9.5 years), and 41% bare ground in burn highlighted in red (dated 5.5 years). Yellow cross indicates location of re-exposed pine stumps >4000 years old (see Figure 4.3.6).

Figure 4.3.6. Example of remains of buried pine stump (dated >4000 years BP) revealed by loss of blanket peat. These stumps were located <300m away from vegetation burns showing very slow vegetation recovery compared to other areas of moorland (Figure 4.3.5).

Figure 4.3.7. Visibly unmanaged ‘wet heath’ in Broomhead catchment (left) and less than 100m distant, Class 1 (new) burn indicating visible effect on surface and subsurface peat layers (right).

4.3.4. Characteristics of API burn Classes 1 to 3

Class 1 (new) burns were found to contain an average of just over 21% vascular plant cover, with the remaining 78.7% existing as exposed peat surface (62.8%) or 'opportunistic' bryophytes (15.9%). For Class 2 (recent) burns, the average vascular cover increases to 77.5% with only 22.5% exposed. Closed canopy Class 3 burns exhibit typically nearly 98% vascular cover (Table 4.3.2).

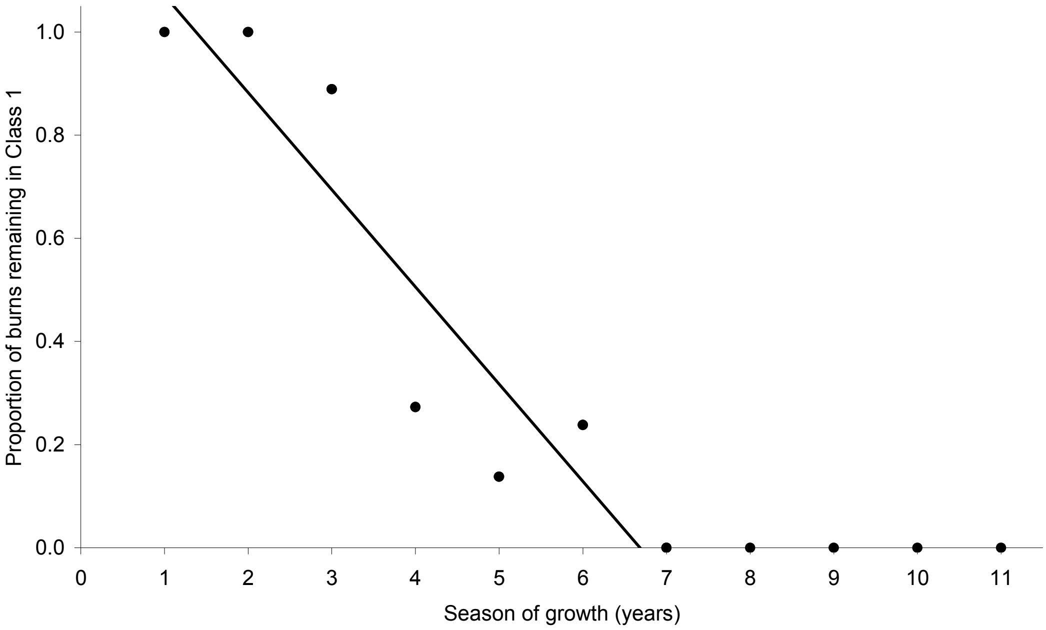
Table 4.3.2. Percent cover of vascular plant, *Calluna* and exposed peat surface by API class, derived from 1 m^2 quadrats (mean and standard error given).

API Class	Number of burns	Vascular plant cover	*Calluna* cover	Exposed peat surface	Potential exposed peat *
1	80	21.3 (2.4)	12.4 (1.4)	62.8 (7.2)	78.7 (9.0)
2	84	77.5 (8.5)	65.2 (7.1)	12.3 (1.3)	22.5 (2.5)
3	17	97.6 (0.8)	90.3 (2.1)	2.4 (0.8)	n/a

(* includes 'opportunistic' bryophyte cover)

As 'survivorship' curves for Class 1 and 2 burns were roughly logistic in form (Figure 4.3.7), trailing 1s and 0s at either end of the curves carried no information and were excluded. Regressions fitted to the approximately linear portion of these curves were used to predict the duration of each class, defined as the length of time for half of the burn scars to move from Class 1 to Class 2 or Class 2 to Class 3. The regression lines for Class 1 (Equation 4.3.1) and Class 2 (Equation 4.3.2) crossed 0.5 at 4.03 years and 8.39 respectively and were taken to be the median end points of these classes.

a)



b)

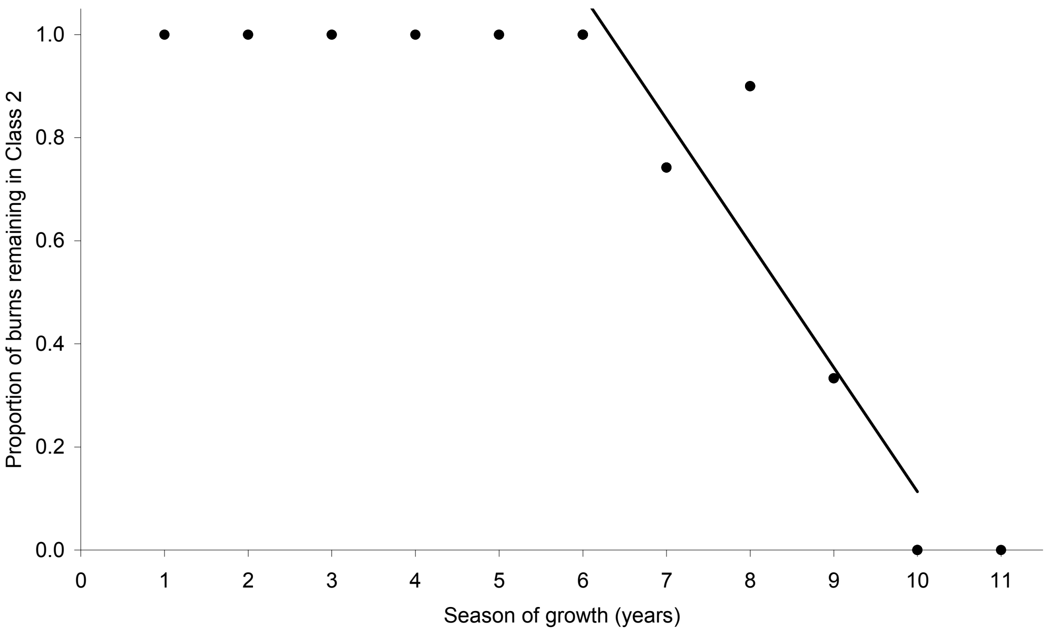


Figure 4.3.8. 'Survivorship' curves for Class 1 (a) and Class 2 (b) burn scars, showing the proportion of burn scars remaining in each class in each season of growth.

$$\text{proportion in Class 1} = 1.259 - 0.188 * \text{season} \qquad (4.3.1)$$

$$\text{proportion in Class 2} = 2.522 - 0.241 * \text{season} \qquad (4.3.2)$$

4.4. Discussion

Calluna regrowth showed a linear increase with age of 3.7 cm yr^{-1} for the burns examined. However, the results also indicate considerable variability in regrowth between burns, but it is not clear whether this is due to pre-burn stand age (Hobbs and Gimingham, 1984b), potential spatial variability in post-fire response or a difference in burn age owing to the length of a burn season (6 months). As no information on pre-burn stand age was available, this was not addressed here. Total vascular plant and *Calluna* cover also increased linearly since date of burn for the exactly dated burns (aged up to 6.5 years), and suggests that variability in growth rates did not have a significant effect on the results here.

The mean area of exposed peat in Class 1 (new) burns was found to be 62.8%, although including 'opportunistic' bryophyte cover (Figure 4.2.1) this increases to 78.7% (Table 4.3.2). This figure is striking considering the median duration of this burn class is estimated to be just over four years (Figure 4.3.8a). Two of the burns surveyed on moorland in Fewston catchment indicate a concerning negative effect of burning on vegetation recovery in some areas of the South Pennines. For these two burns, aged 5.5 and 9.5 years old, the area of exposed peat surface was found to be 41% and 20% respectively. Compared to other areas of moorland surveyed in this research, vegetation recovery is far slower in this area and the peat surface remains exposed for longer periods of time. Exposure of peat surface following severe wildfire has been implicated in the initiation of blanket peat erosion and gully formation (Yeloff *et al*., 2006), and it is interesting to note that 300 m away from the two poorly recovering burns, buried pine stumps aged >4000 years BP have been re-exposed. This suggests that in this area, controlled burning may have contributed to enhanced loss of blanket peat through oxidative or erosive processes. Initiation of such detrimental processes as suggested by Yeloff *et al*. (2006) may also be visibly evident in burns found in Broomhead catchment (Figure 4.3.7).

Blanket peats in the UK formed in blanket bogs (Lindsay, 1995) of predominantly *Sphagnum*-rich moss communities. However the absence of *Sphagnum spp*. from 95% (1587) of the quadrats surveyed indicates that the areas surveyed in the South Pennines are dysfunctional bog systems. Whether the observations here result from controlled burning (Pearsall, 1941; Bragg and Tallis, 2001) or increased airborne pollutant deposition (Proctor, 1997) is however not clear.

4.5. Conclusion

The percent cover of vegetation and exposed peat surface of API burn Classes 1 and 2 on blanket peat, and the median duration of each class were determined. These figures provide key insight for the interpretation of the results presented in Chapters 5 to 8.

Chapter 5 – Spatial variation in DOC production and release from upland peat soils I: field sampling of small headwater catchments

5.1 Introduction

Upland catchments in the UK exhibit widespread variation in DOC production and release (e.g. Monteith and Evans, 2005). Stream discharge (Grieve, 1984), catchment slope (e.g. Aitkenhead *et al*., 1999) and altitude (Hope *et al*., 1997a) have been shown to influence DOC concentrations in drainage, yet a greater degree of variance in DOC can be explained by the percent cover of blanket or deep peat within catchments (e.g. McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001). However, more localised differences in DOC release at variance with these observations have been found in many small upland catchments (Yallop *et al*., 2008). Increasing trends in DOC concentrations have also been observed in surface waters draining areas of upland peat (e.g. Freeman *et al*., 2001a; Worrall *et al*., 2003b; Evans *et al*., 2005). Numerous drivers of increased DOC production have been proposed, including hydrological change (Evans *et al*., 2005), elevated atmospheric CO_2 (Freeman *et al*., 2004), and severe drought (Worrall and Burt, 2004). Decreasing atmospheric acid deposition has also been implicated (Evans *et al*., 2006) and this may be important as a driver of increases in DOC globally (Monteith *et al*., 2007). However, none of these factors appear obvious candidates to explain local or small-scale spatial variation in patterns of DOC release, a suggestion supported by observations of Worrall and Burt (2007) that DOC release from upland peat catchments does not correlate well with changes in either acid deposition or occurrences of severe drought in the UK.

In the UK, upland areas have a complex history of human occupation, land use and management, activities that do vary at fine spatial scales and could therefore provide potential localised drivers of environmental change, over and above those that may be occurring at a larger scale. Many areas of upland blanket peat, particularly in the English Pennines, were extensively drained in the 1960s and 1970s (Holden *et al.*, 2004) and currently livestock grazing and controlled burning for red grouse game shooting are the most extensive forms of management (Simmons, 2003). The hydrological effects of drainage appear mixed, as earlier studies (e.g. Stewart and Lance, 1991) suggest that artificial drains tend to affect water tables within only a few metres either side of the channel. More recent work (Holden *et al.*, 2006), however, suggests that increased drainage has cumulative effects that are significant in the long term and Wallage *et al.* (2006) identified higher interstitial DOC concentrations in drained peat catchments. To date there is little evidence to suggest that grazing has any direct effect on DOC although the consequences of burn management have been studied. Under well-managed rotational burns, interstitial DOC concentrations may be lower (Worrall *et al.*, 2007) although accelerated surface erosion, increased infiltration and throughflow (Imeson, 1971), more extreme and variable temperatures (Fullen, 1983), increased porosity (Mallik and Fitzpatrick, 1996) and reduced carbon sequestration (Garnett *et al.*, 2000) have all been found on moorland under burning management. Although not quantified, Mitchell and McDonald (1992) noted higher colour in surface waters draining from catchments with extensive burning and Yallop *et al.* (2008) found a highly significant relationship between the extent of burn management on blanket peat and water colour (Hazen) in drainage waters.

Factors controlling carbon loss from upland peat soils and the spatial variance in DOC concentrations observed in the UK are not well understood. This chapter aims to investigate any relationships between land use/management and drainage DOC concentrations for a series of upland peat catchments in the South Pennines and on the North Yorkshire Moors. The objectives for this chapter were defined as:

i. identify and select a series of upland peat catchments in the South Pennines and on the North Yorkshire Moors;
ii. obtain aerial imagery covering the extent of the study catchments;
iii. derive land use/management statistics and physical catchment descriptors for the selected catchments;
iv. collect water samples from the study catchments over the course of a year;
v. identify any relationships between land use and catchment descriptors and DOC concentrations.

5.2 Methods

5.2.1 Selection of study catchments

Ordnance Survey Panorama 1:50 000 digital terrain models (DTMs) were obtained for the extent of the South Pennines and North Yorkshire Moors. The hydrological data model ArcHydro, an extension for GIS software ArcGIS (Maidment, 2002), was used to delineate potential study catchments from these data. Processing of DTMs with this tool allows rapid extraction of drainage catchments for any spatial location selected within the data, based primarily on a function of elevation and slope. Access to potential water sampling locations was a key factor during catchment generation, as this would impact on the timeframe for collection of dispersed samples and sample storage prior to analysis. Owing to the source of funding for this research, catchment selection was primarily restricted to areas of moorland owned or operated by Yorkshire Water.

An initial set of 150 catchments (typically smaller than 3 km^2) were defined for high-order drainage channels that fell within upland habitats as defined by Natural England digital vector data (Upland Heathland and Blanket Bog habitat boundaries v1.1; Natural England, 2005). As the primary source of DOC to upland drainage water is blanket peat, with secondary contribution from thin peats (McDonald *et al*., 1991), catchments containing less than a minimum area of 25% raw peats or soils with peaty horizons (according to National Soil Resource Institute (NSRI) digital soil data derived from Mackney *et al*. (1983)) were excluded. This subset was then further refined by selecting catchments that clustered within 20 km of each other to minimise effects arising from local meteorological or acid depositional differences between them. This produced a total of 50 catchments, ranging in size from 0.13 to 3 km^2, grouped in four discrete areas: North Yorkshire Moors, and North, South and West Yorkshire (Figure 5.2.1). This catchment selection included ten catchments previously studied by Yallop *et al*. (2008). Mean catchment area and slope were derived from the DTMs for the 50 catchments using ArcGIS.

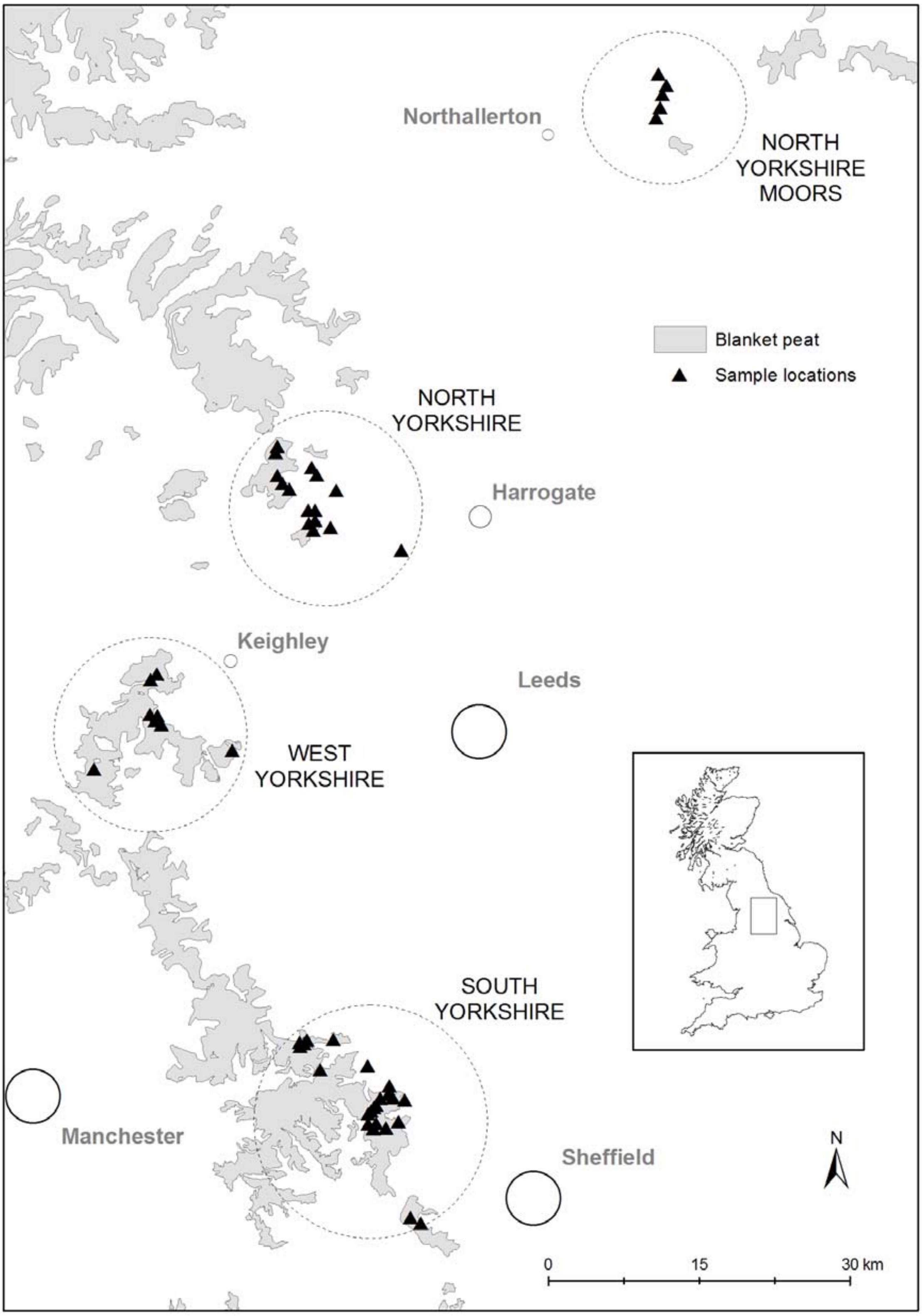


Figure 5.2.1. Water sample locations selected for analysis of spatial variation in DOC concentration.

5.2.2. Land use/management and soil distribution

25 cm resolution colour aerial photography for all catchments was captured in 2005 and orthocorrected (see Chapter 3.2.1). Land cover classes identifiable across all catchments, namely unimproved grassland, semi-improved grassland, coniferous plantation, ericaceous dominated (predominantly *Calluna*) and grass/sedge dominated moorland were mapped for each catchment using ArcGIS. Areas of vegetation burn Class 1 (new burn), Class 2 (recent burn) and Classes 3 and 4 (closed canopy heath) (see Chapter 3.2.2) were mapped within areas of *Calluna* dominated moorland.

Soils present within each catchment were identified by intersecting digital soil data with catchment boundaries. These were subsequently categorised into three broad soil types: blanket peat; upland soils with peaty horizons; and non-peaty soils (Table 5.2.1), following the descriptions given by Avery (1980). The areal extent of all combinations of land use, management and soil type present in each catchment were then derived using ArcGIS and converted to proportions. Variables that accounted for less than 1% of a catchment were rounded to zero and subsequently those that occurred in two or less catchments were excluded from analysis (Table 5.2.2).

Table 5.2.1. Soils present in catchments categorised into broad soil type following descriptions by Avery (1980).

Soil type	Blanket peat	Upland soils with peaty horizons	Non-peaty soils
Soil group	*Raw peat soils*	*Stagnopodzols*	*Non-calcareous pelosols*
Soil sub-groups	1011b	651a; 652	421a
		Stagnohumic gley soils	*Brown earths*
		721b, c	541f,g, y
			Podzols
			631a
			Stagnogley soils
			711p; 713g

Table 5.2.2. Percent land use, management and soil type combinations for each catchment.

Study area	Area (km^2)	Slope (degrees)	Gripped	Soil type			Grass / sedge moorland		Unimproved grass	*Calluna* moorland		Improved grass		Plantation	Class 1 Burn			Class 2 Burn		Closed canopy heath Class 3&4	
		Soil type		BP	NP	PH	BP	PH	NP	BP	PH	NP	PH	PH	BP	PH	AL	BP	PH	BP	PH
SY†	0.48	7.34		75	0	25	0	06	0	74	20	0	0	0	22	05	27	26	03	26	12
SY†	0.86	7.42		20	22	58	02	32	03	18	15	13	11	0	05	0	05	03	0	10	15
SY†	1.40	4.06		98	0	02	05	01	0	93	0	0	0	0	33	0	33	17	0	43	0
SY†	2.00	4.78		97	0	03	12	02	0	85	0	0	0	0	27	0	27	16	0	43	0
SY	0.42	4.73		94	0	06	37	06	0	57	0	0	0	0	16	0	16	02	0	39	0
SY	0.25	2.75		100	0	0	12	0	0	88	0	0	0	0	19	0	19	03	0	66	0
SY†	2.24	4.38		100	0	0	13	0	0	87	0	0	0	0	30	0	30	18	0	39	0
SY	0.31	5.17		100	0	0	04	0	0	96	0	0	0	0	36	0	36	26	0	33	0
SY	0.43	4.22		100	0	0	05	0	0	95	0	0	0	0	35	0	35	27	0	33	0
SY	1.42	4.22		100	0	0	18	0	0	82	0	0	0	0	26	0	26	13	0	43	0
SY	1.19	6.98		96	0	04	13	04	0	83	0	0	0	0	24	0	24	20	0	39	0
SY	0.57	4.71		0	77	23	0	0	0	0	0	50	0	22	0	0	0	0	0	0	0
SY	0.55	8.29		68	0	32	40	18	0	28	14	0	0	0	03	03	6	05	05	20	6
SY	0.39	5.61		0	0	100	0	09	0	0	40	0	51	0	0	13	16	0	12	32	3
SY	1.23	6.98		85	0	15	26	09	0	59	06	0	0	0	16	0	13	11	02	0	15
SY	1.64	4.72		38	0	62	25	36	0	12	10	0	07	09	02	01	03	05	05	5	4
SY	1.90	4.01		93	0	07	09	02	0	84	05	0	0	0	19	0	19	30	03	35	1
SY	0.15	6.99		23	0	77	23	77	0	0	0	0	0	0	0	0	0	0	0	0	0
SY	0.41	4.33	*	71	0	29	21	21	0	50	08	0	0	0	23	05	27	10	02	17	2
SY	0.13	5.75		14	0	86	0	37	0	13	49	0	0	0	06	42	47	07	07	0	0
SY	0.72	7.50		55	0	45	55	45	0	0	0	0	0	0	0	0	0	0	0	0	0
WY	0.64	5.29		100	0	0	63	0	0	37	0	0	0	0	14	0	14	0	0	22	0
WY	0.68	5.52		100	0	0	61	0	0	39	0	0	0	0	15	0	15	01	0	23	0
WY†	0.21	4.94		100	0	0	06	0	0	94	0	0	0	0	19	0	19	17	0	56	0
WY†	0.54	3.75		100	0	0	35	0	0	65	0	0	0	0	02	0	02	02	0	61	0
WY†	0.30	7.89		100	0	0	08	0	0	92	0	0	0	0	04	0	04	0	0	88	0
WY†	0.41	7.13		63	0	37	58	37	0	05	0	0	0	0	0	0	0	0	0	5	0
WY†	0.38	6.46		22	0	78	17	55	0	05	22	0	0	0	0	0	0	0	0	5	22
WY	0.57	6.50		85	0	15	24	06	0	60	10	0	0	0	0	0	0	03	04	57	5
WY	0.36	3.70		35	0	65	18	13	0	0	0	0	52	0	0	0	0	0	0	0	0
NY	3.02	4.87	*	0	13	87	0	29	05	0	34	09	24	0	0	13	13	0	10	0	11
NY	1.50	4.68	*	0	0	100	0	29	0	0	31	0	41	0	0	10	10	0	10	0	11
NY	1.94	6.16	*	26	0	74	04	53	0	22	18	0	04	0	04	09	13	10	04	8	5
NY	0.52	4.14	*	25	0	75	04	43	0	21	33	0	0	0	05	15	20	08	08	8	9
NY	1.27	4.96	*	05	04	91	0	41	04	05	50	0	0	0	01	13	14	03	16	2	20
NY	0.37	3.70	*	33	0	67	02	26	0	31	41	0	0	0	06	13	19	19	08	5	20
NY	2.55	4.12		0	0	100	0	50	0	0	0	0	50	0	0	0	0	0	0	0	0
NY	0.56	3.46	*	100	0	0	05	0	0	95	0	0	0	0	23	0	23	39	0	33	0
NY	0.51	4.65	*	0	22	78	0	78	22	0	0	0	0	0	0	0	0	0	0	0	0
NY	1.63	5.05	*	62	0	37	18	12	0	44	16	0	09	0	11	03	14	10	02	24	11
NY	0.47	4.63	*	0	63	37	0	26	63	0	11	0	0	0	0	04	04	0	01	0	6
NY	0.74	4.06	*	100	0	0	77	0	0	23	0	0	0	0	07	0	07	05	0	11	0
NY	0.93	5.78		0	0	100	0	34	0	0	05	0	46	15	0	01	01	0	02	0	2
NY	0.73	4.08		65	0	35	09	12	0	56	23	0	0	0	02	06	08	13	01	41	16
NY	1.60	5.29		71	0	29	15	08	0	55	21	0	0	0	09	06	14	08	03	38	13
NYM	1.42	3.72		0	0	100	0	13	0	0	87	0	0	0	0	15	15	0	51	0	21
NYM	1.82	4.67		0	0	100	0	09	0	0	91	0	0	0	0	31	31	0	37	0	23
NYM	0.62	5.49	*	0	0	99	0	15	0	0	84	0	0	0	0	31	31	0	31	0	21
NYM	1.02	5.03		0	08	92	0	10	06	0	68	01	13	0	0	17	17	0	35	0	16
NYM	1.64	7.74		0	05	95	0	14	04	0	57	0	0	25	0	11	11	0	18	0	27

(† Catchments studied in Yallop *et al*. (2008). BP – blanket peat; PH – soils with peaty horizon; NP – non peaty soil; AL – ALL soil types; SY – South Yorkshire; WY – West Yorkshire; NY – North Yorkshire; NYM – North Yorkshire Moors; * indicates presence of gripping).

5.2.3. Artificial drainage

Assessing the potential influence of artificial drainage (gripping) on drainage DOC concentration (e.g. Wallage *et al*., 2006) is not straightforward. There are no existing classification schemes for the interpretation of artificial drainage from aerial imagery, and these might need to account for several characteristics:

- the age of a grip;
- the density and length of channels;
- the style (hard or soft ditching i.e. across or along contours (McDonald *et al*., 1991));
- the type (whether the ditch cuts through surface peat or subsequent erosion has exposed mineral soil or bedrock at the base);
- grip blocking (natural blocking following slumping of sides or artificial installations).

Several of these characteristics cannot be determined from aerial imagery. Therefore the presence of gripping visible in aerial photography was recorded for all catchments (Table 5.2.2), and a separate analysis of gripped and non-gripped catchments was undertaken.

5.2.4. Water sampling and analysis

As there is significant seasonal variation in DOC concentration within upland drainage waters (e.g. Grieve, 1984, 1991; Scott *et al*., 1998), water samples were collected from the study catchments on four occasions in 2005. As 42 of the study catchments contain areas of moorland managed for red grouse, and restrictions to permitted access occur during the breeding season (April to June) and early in the shooting season (August to December), water sampling was undertaken in January, March, November and December. All catchments within each of the four defined study areas were sampled within 24 hours to minimise as far as practical any responses to differing meteorological conditions, and all four areas were sampled within a five day period. Of the 50 catchments examined, difficulties with access during part of the year were still experienced and water sampling was only possible at 39 in January and 42 in March.

In each sample period, two 50 ml samples were collected for each catchment. Sample bottles were filled to remove the air gap and thus reduce potential dissolution of carbon dioxide into samples with acidic pH. During transport samples were stored in an ice box. Prior to analysis, samples were filtered through Whatman 0.45 μm cellulose filter membranes, and stored in the dark at 4°C. All analysis was undertaken within 14 days of sample collection, during which time degradation of DOC is unlikely to be significant as Mitchell and McDonald (1992) report a 5% reduction in colour for samples stored at 8°C over this time period. DOC concentration was determined by persulphate-ultraviolet (UV) oxidation using the method described by Clesceri *et al*. (1998) (see Chapter 3.3).

5.2.5. Meteorological effects during sampling

DOC concentrations in upland drainage have been related to stream discharge (e.g. Grieve, 1984), and antecedent rainfall prior to sampling could therefore introduce bias in the DOC concentrations measured in this study owing to the spatial extent over which sampling was conducted. Rainfall data for calendar year 2005 were obtained from the British Atmospheric Data Centre (http://badc.nerc.ac.uk) for the meteorological station nearest to each sample catchment. As all samples were collected over a five day period, the cumulative rainfall for the seven days prior to sampling for each catchment was determined (Table 5.2.3).

5.2.6 Statistical analysis

The potential influence of rainfall on measured DOC concentrations was assessed by regressing rainfall for the seven days prior to sampling for each catchment against DOC concentration in each sampling period. Several approaches were then adopted to identify any relationships between land use and DOC concentration in drainage waters:

- To examine any overall relationship between land use and DOC concentrations, independent of short-term variations as far as possible, data from each sampling period were firstly pooled to produce a mean DOC concentration for each sample catchment. Owing to problems gaining access to some sample catchments in January and March, analysis could only be performed using four-monthly sample means (Jan, Mar, Nov and Dec) for 39 catchments and a mean of two months (Nov and Dec) for the full 50 catchments.
- Geographic variation in DOC between the four sample regions was then examined by pooling data from the sample catchments within each study region. To ensure adequate samples for analysis, all samples collected for each site were used and therefore seasonal variation was not accounted for.
- Seasonal variation in any relationships between land use and DOC release was explored by pooling data from the four regions for each sampling period.
- As the proportion of blanket peat within a catchment has already been linked to DOC release (Aitkenhead *et al*., 1999), those sites covered by <85% blanket

peat were excluded to examine the role of land management on predominantly blanket peat catchments.

- Drainage alters soil hydrology and could modify DOC production (Wallage *et al*., 2006), therefore catchments containing visible artificial drainage were excluded, and analysis of covariance performed to test for any difference in the regression models for land use and DOC between gripped and non-gripped catchments.
- As ten of the catchments included in this study have previously been examined by Yallop *et al*. (2008), the significance of these catchments in driving any relationships identified between land use and DOC across all catchments was examined. The ten catchments were excluded, and analysis of covariance performed to test for any difference in the regression models for land use and DOC between the two groups of catchments.

In all analyses, catchment area, mean slope and a total of 18 land use/management/soil type variables (Table 5.2.2) were regressed against DOC concentration using forward-entry stepwise multiple regression. Variables were normalised prior to regression analysis using the arcsine-square root transformation (Fowler and Cohen, 1990). As the number of variables examined was high, conditions for inclusion in the regression were improvements in the model set at $p<0.01$. Analysis was undertaken using SPSS v.15.0.

Table 5.2.3. Rainfall prior to sampling and measured DOC concentrations for all catchments.

Study area	Mean rainfall prior to sampling (7 days)					DOC concentration (mg l^{-1})					
	Distance to rain gauge (km)	Rainfall prior to Jan (mm)	Rainfall prior to Mar (mm)	Rainfall prior to Nov (mm)	Rainfall prior to Dec (mm)	January	March	November	December	4 month mean	2 month mean
SY	4.38	13.2	9.1	2.2	41.1	15.40	7.70	6.30	31.30	15.18	18.80
SY	2.46	16.3	10.7	3.2	48.7	5.30	5.30	4.35	7.15	5.53	5.75
SY	4.54	16.3	10.7	3.2	48.7	26.80	23.30	26.30	27.40	25.95	26.85
SY	4.47	16.3	10.7	3.2	48.7	28.10	21.00	29.80	28.30	26.80	29.05
SY	5.37	*n.s.*	*n.s.*	3.2	48.7	*n.s.*	*n.s.*	20.85	22.50	-	21.68
SY	5.45	*n.s.*	*n.s.*	3.2	48.7	*n.s.*	*n.s.*	25.20	29.20	-	27.20
SY	3.47	16.3	10.7	3.2	48.7	22.70	15.60	22.95	25.70	21.74	24.33
SY	3.47	*n.s.*	*n.s.*	3.2	48.7	*n.s.*	*n.s.*	33.70	30.20	-	31.95
SY	3.73	*n.s.*	*n.s.*	3.2	48.7	*n.s.*	*n.s.*	26.40	26.85	-	26.63
SY	4.06	*n.s.*	*n.s.*	3.2	48.7	*n.s.*	*n.s.*	21.35	25.55	-	23.45
SY	1.95	27.6	10.7	3.2	52.6	11.70	6.10	11.00	20.95	12.44	15.98
SY	1.78	27.6	10.7	4.4	48.7	7.60	8.30	6.25	11.15	8.33	8.70
SY	1.56	16.3	10.7	3.2	52.6	5.60	8.10	5.10	6.80	6.40	5.95
SY	0.96	27.6	10.7	3.2	52.6	3.60	4.60	1.80	6.60	4.15	4.20
SY	1.55	n.s.	10.7	3.2	52.6	n.s.	9.60	4.35	8.70	-	6.53
SY	1.43	30.1	4.7	5.0*	52	7.50	7.20	6.25	14.90	8.96	10.58
SY	2.28	30.1	4.7	5.0*	52	7.50	7.90	5.70	21.50	10.65	13.60
SY	2.10	50.9	18.6	6.2	62.2	2.50	3.50	5.65	8.20	4.96	6.93
SY	1.72	50.9	18.6	6.2	62.2	8.30	10.60	11.55	17.15	11.90	14.35
SY	0.59	39.5	12	6.9	74.7	11.60	15.00	7.15	18.05	12.95	12.60
SY	1.89	39.5	12	6.9	74.7	4.40	4.30	3.35	8.40	5.11	5.88
WY	4.67	40.9	15.2	3.6	44.2	*n.s.*	21.80	28.70	19.20	-	23.95
WY	4.67	40.9	15.2	3.6	44.2	*n.s.*	21.60	25.35	18.65	-	22.00
WY	2.30	38.5	16.2	2.1	39.6	9.10	16.70	7.25	13.70	11.69	10.48
WY	1.27	38.5	16.2	2.1	39.6	5.90	13.70	9.05	14.50	10.79	11.78
WY	2.36	40.9	15.2	3.6	44.2	6.90	11.10	21.55	14.90	13.61	18.23
WY	2.03	40.9	15.2	3.6	44.2	4.10	6.30	4.85	8.30	5.89	6.58
WY	2.28	38.5	16.2	2.1	39.6	5.30	4.60	3.00	4.70	4.40	3.85
WY	1.78	38.5	16.2	2.1	39.6	7.40	8.90	6.05	6.75	7.28	6.40
WY	8.94	40.9	15.2	3.6	44.2	14.80	9.80	12.05	13.75	12.60	12.90
NY	0.57	26.6	14.5	0.5	43.2	10.70	7.30	3.85	12.05	8.48	7.95
NY	1.25	*n.s.*	*n.s.*	0.5	43.2	*n.s.*	*n.s.*	6.25	8.35	-	7.30
NY	1.44	26.6	14.5	0.5	43.2	9.00	6.10	4.20	10.40	7.43	7.30
NY	2.70	*n.s.*	*n.s.*	0.5	43.2	*n.s.*	*n.s.*	9.95	15.30	-	12.63
NY	2.35	26.6	14.5	0.5	43.2	6.40	5.80	3.65	6.80	5.66	5.23
NY	2.81	*n.s.*	*n.s.*	0.5	43.2	*n.s.*	*n.s.*	7.30	11.45	-	9.38
NY	8.78	26.6	14.5	0.5	43.2	10.70	7.30	8.25	10.10	9.09	9.18
NY	6.63	29.7	16.6	0	39.3	12.20	22.20	14.15	24.65	18.30	19.40
NY	2.32	26.6	14.5	0.5	43.2	11.40	10.90	6.55	8.35	9.30	7.45
NY	3.05	26.6	14.5	0.5	43.2	13.30	13.60	10.70	15.30	13.23	13.00
NY	0.78	26.6	14.5	0.5	43.2	8.70	10.70	7.05	10.20	9.16	8.63
NY	5.74	29.7	16.6	0	39.3	9.00	15.10	8.55	14.90	11.89	11.73
NY	3.03	26.6	14.5	0.5	43.2	10.90	12.80	11.70	12.45	11.96	12.08
NY	4.30	26.6	14.5	0.5	43.2	8.60	9.30	6.60	9.55	8.51	8.08
NY	4.53	26.6	14.5	0.5	43.2	12.40	15.10	11.25	17.65	14.10	14.45
NYM	2.24	5.0	6.6	0.3	24.9*	3.80	8.90	3.50	9.40	6.40	6.45
NYM	2.89	5.0	6.6	0.3	24.9*	2.80	7.20	2.05	5.50	4.39	3.78
NYM	3.18	5.0	6.6	0.3	24.9*	3.00	7.10	4.00	6.15	5.06	5.08
NYM	1.70	5.0	6.6	0.3	24.9*	4.20	10.00	3.95	6.00	6.04	4.98
NYM	1.80	5.0	6.6	0.3	24.9*	2.20	5.60	3.20	5.25	4.06	4.23

(*n.s.* catchment not sampled owing to access restrictions. * - missing data, values taken from next closest gauge).

5.3. Results

5.3.1. Overall relationship between land use and DOC concentration

No significant relationships were identified between rainfall for the seven days prior to sampling and measured DOC concentrations for any of the four sampling periods, indicating that any localised variations in rainfall were minor and not significantly influencing further results.

Of the 18 land use/soil combinations, catchment area and slope factors tested in the forward-entry multiple regression, the proportion of new burn (Class 1) on blanket peat was identified as the most significant predictor of DOC concentration in both four-month (r^2=0.62, p<0.001, 39 sample catchments, Figure 5.3.1) and two-month analyses (r^2=0.69, p<0.001, 50 sample catchments, Figure 5.3.2) (Table 5.3.1). In the two-month analysis, the proportion of recent burn (i.e. Class 2) on blanket peat was also added to the regression model, increasing the degree of variance explained from r^2=0.69 to 0.77 (Table 5.3.1).

To determine the direct influence of the proportion of blanket peat (soil type 1011b) in each catchment on DOC concentration, a single ‘forced’ linear regression of the proportion of blanket peat against DOC was then also performed. In both cases, i.e. using 39 sample catchments (four-month) and 50 samples catchments (two-month), the regression was highly significant (p<0.001, Table 5.3.1).

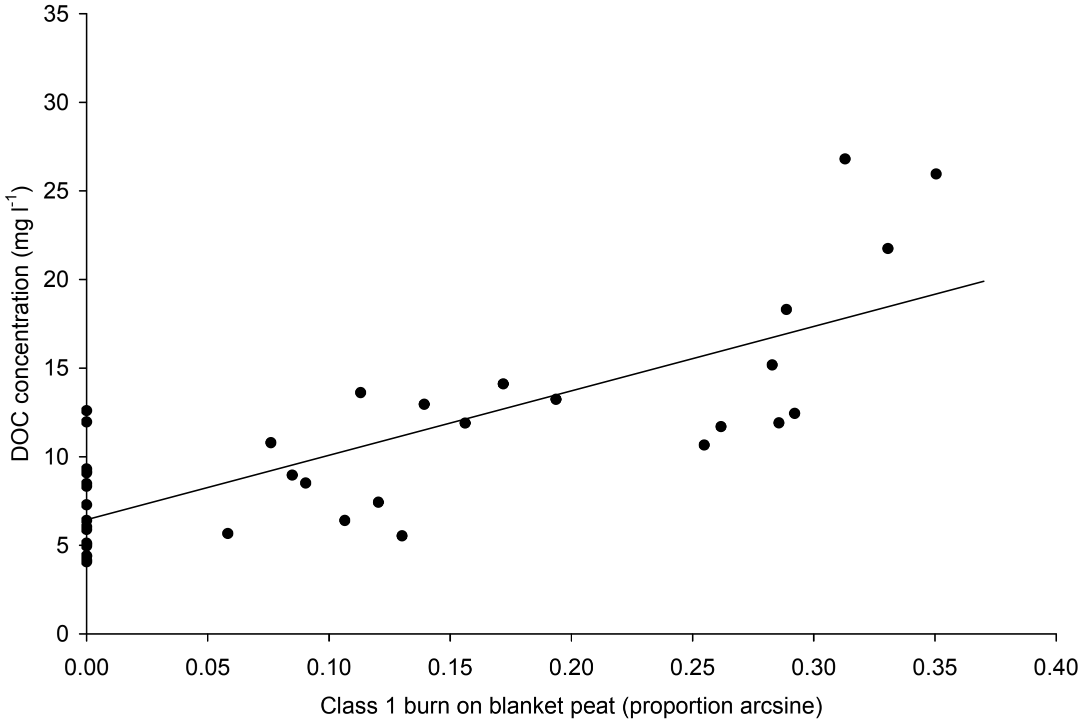


Figure 5.3.1. Proportion of catchment as Class 1 burn on blanket peat against four-month mean (Jan, Mar, Nov and Dec) DOC concentration in 2005 (r^2=0.62, *p*<0.001, n=39).

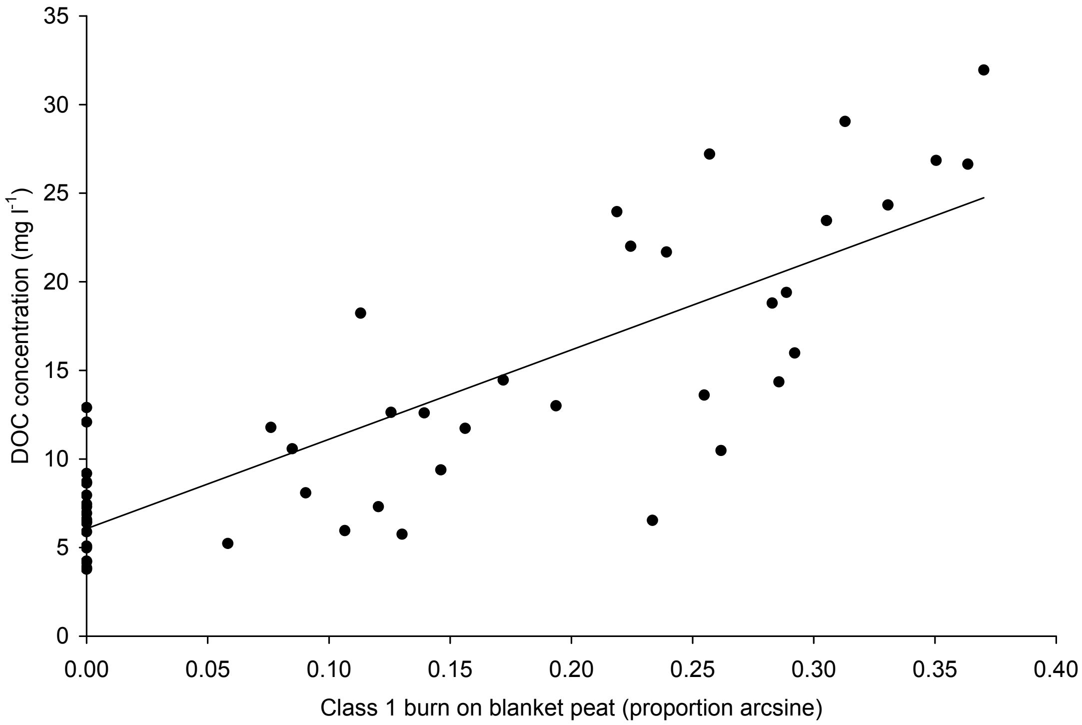


Figure 5.3.2. Proportion of catchment as Class 1 burn on blanket peat against two-month mean (Nov and Dec) DOC concentration in 2005 (r^2=0.69, *p*<0.001, n=50).

Table 5.3.1. Predictors of DOC concentration for study catchments identified using forward-entry multiple regression.

Analysis	n	Primary predictor	r^2	Second variable entered	r^2	Blanket peat †
All catchments						
Jan, Mar, Nov and Dec mean	39	Burn Cl1 on blanket peat	0.62 ***			0.37 ***
Nov and Dec mean	50	Burn Cl1 on blanket peat	0.69 ***	Burn Cl2 on blanket peat	0.77 ***	0.54 ***
Regional						
South Yorkshire	72	Burn Cl1 on blanket peat	0.54 ***	Closed canopy *Calluna* on peaty soil ɣ	0.60 ***	0.46 ***
West Yorkshire	33	Burn Cl1 on blanket peat	0.40 ***	Burn Cl2 on blanket peat	0.58 ***	0.29 **
North Yorkshire	53	Burn Cl1 on blanket peat	0.32 ***	*Calluna* on peaty soil ɣ	0.41 ***	0.27 ***
North Yorkshire Moors	25	None				None
Seasonal						
January 2005	39	Burn Cl1 on blanket peat	0.45 ***			0.19 **
March 2005	42	Burn Cl1 on blanket peat	0.38 ***			0.35 ***
November 2005	50	Burn Cl1 on blanket peat	0.51 ***	Burn Cl2 on blanket peat	0.70 ***	0.46 ***
December 2005	50	Burn Cl1 on blanket peat	0.74 ***			0.50 ***
>85% blanket peat catchment						
Jan, Mar, Nov and Dec mean	11	Burn Cl1 on blanket peat	0.50 **			
Nov and Dec mean	19	Burn Cl1 on blanket peat	0.46 ***			

***p<0.001; **p<0.01;
† result from single linear regression
ɣ shows an inverse relationship to DOC

5.3.2. Regional analysis

Examining each region separately showed that for each of the three Pennine regions examined, the most significant predictor of DOC concentration was the proportion of new burn (Class 1) on blanket peat within the catchment (Table 5.3.1). This positive relationship was highly significant in each of these three regions ($p<0.001$) and the degree of variance explained varied from $r^2=0.32$ (North Yorkshire, 15 sample catchments; Figure 5.3.3), $r^2=0.40$ (West Yorkshire, nine sample catchments; Figure 5.3.4) to $r^2=0.54$ (South Yorkshire, 21 sample catchments; Figure 5.3.5). In each case a second variable entered into the regression model, which in the case of West Yorkshire was the proportion of recent burn (Class 2) on blanket peat, improving the model's r^2 from 0.40 to 0.58. In North Yorkshire the proportion of total *Calluna* moorland on soils with peaty horizons was added, improving the model r^2 from 0.32 to 0.41. In the South Yorkshire catchments, closed-canopy *Calluna* moorland (burn classes 3 and 4) was entered in the regression improving the model r^2 from 0.54 to 0.60. It should be noted however that these latter two factors showed an inverse relationship with DOC. No significant relationships between any of the tested variables and DOC were identified for the North Yorkshire Moors sample catchments.

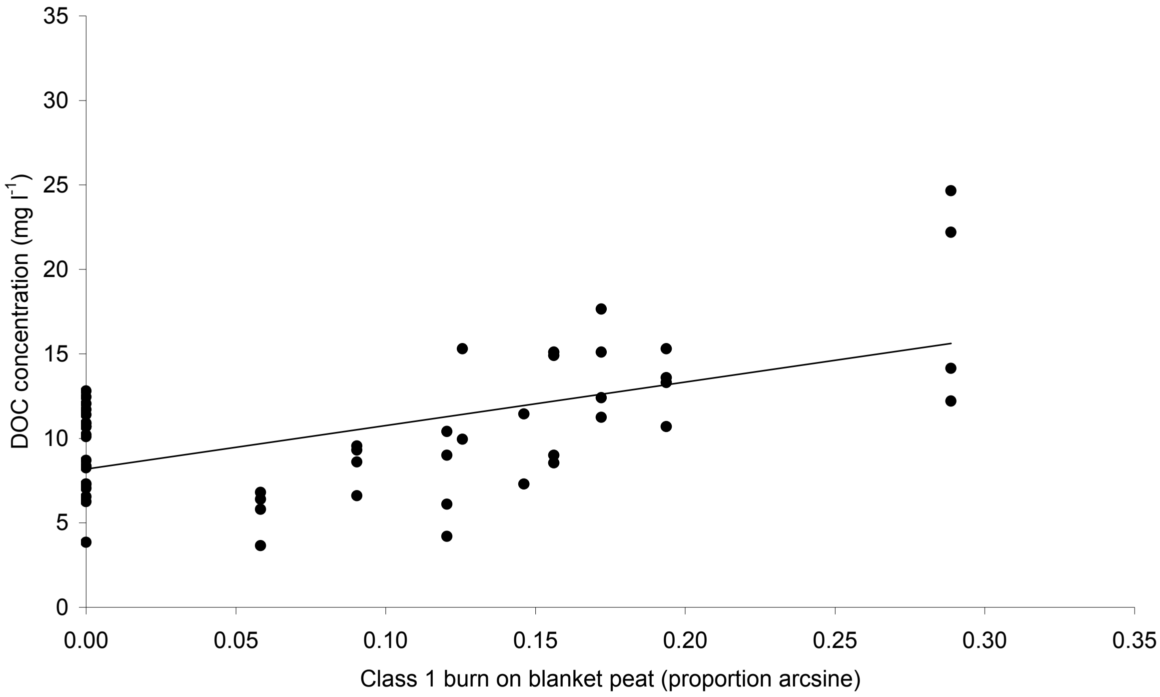


Figure 5.3.3. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for 15 catchments located in North Yorkshire sampled in 2005 (r^2=0.32, *p*<0.001, n=53).

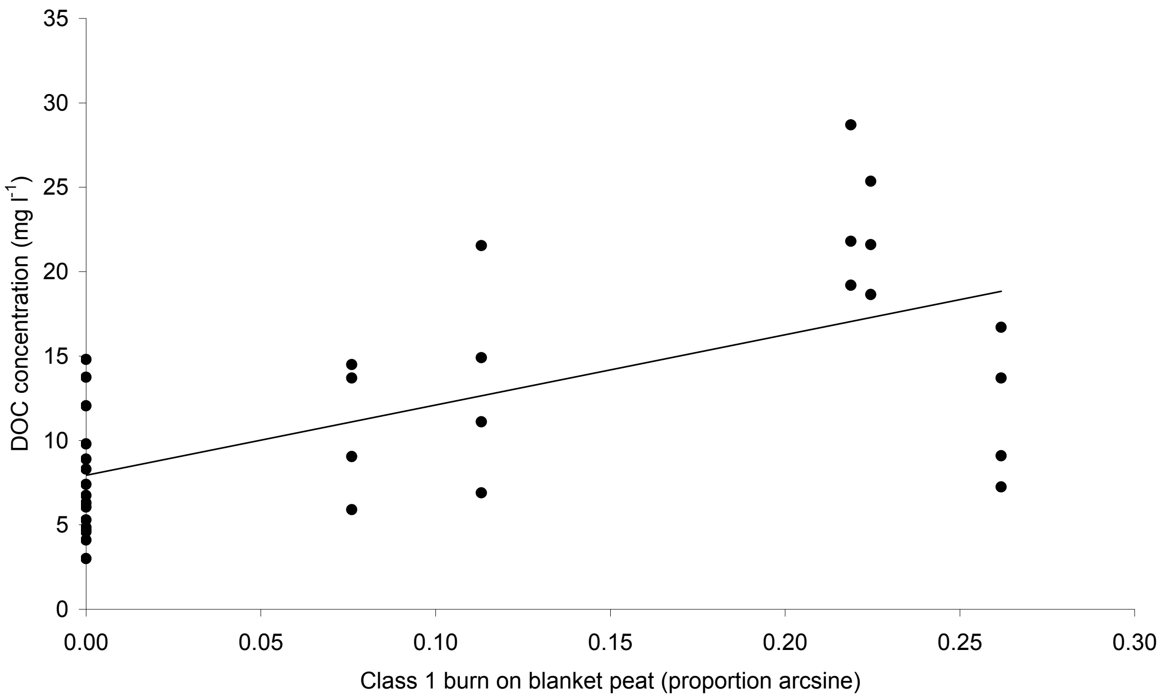


Figure 5.3.4. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for nine catchments located in West Yorkshire sampled in 2005 (r^2=0.40, *p*<0.001, n=33).

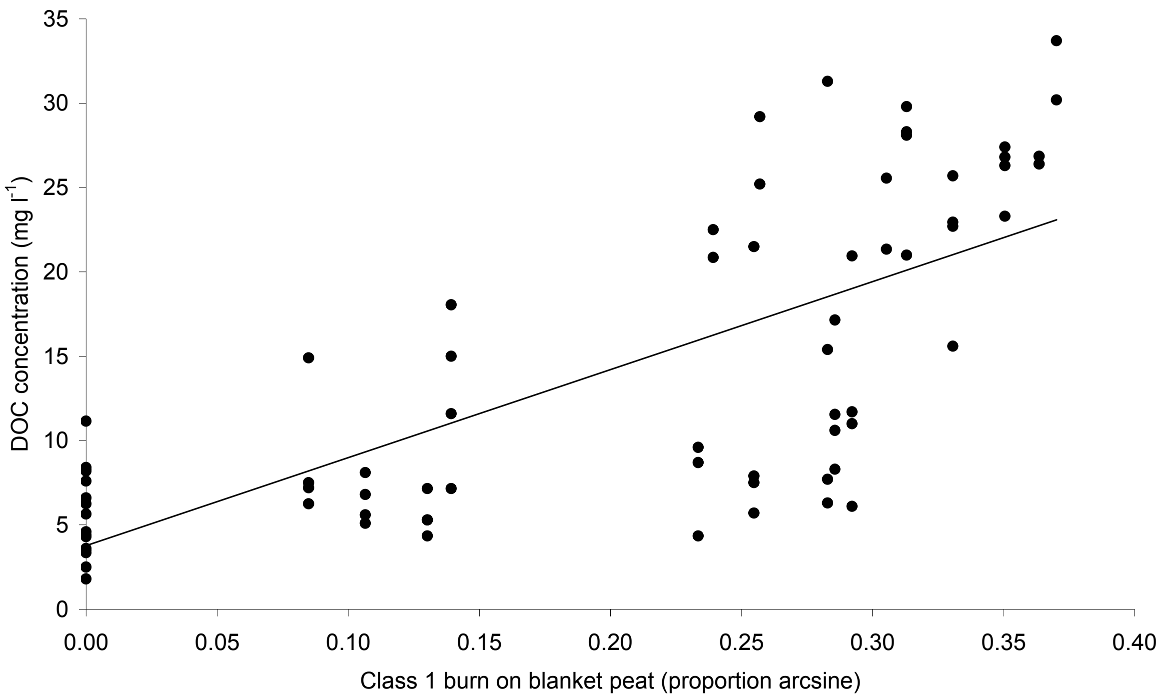


Figure 5.3.5. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for 21 catchments located in South Yorkshire sampled in 2005 (r^2=0.54, p<0.001, n=72).

5.3.3. Seasonal analysis

In each sampled month, the most significant predictor of DOC concentration identified in multiple regression was the proportion of new burn (Class 1) on blanket peat (Table 5.3.1). The relationship was highly significant in each month (p<0.001) with the proportion of variance explained varying from r^2=0.38 (March, 42 sample catchments; Figure 5.3.6), r^2=0.45 (January, 39 sample catchments; Figure 5.3.7), r^2=0.52 (November, 50 sample catchments; Figure 5.3.8) to r^2=0.74 (December, 50 sample catchments; Figure 5.3.9). In the analysis of data for November, the proportion of recent burn (Class 2) on blanket peat also entered into the regression, improving the model fit from r^2=0.52 to 0.70.

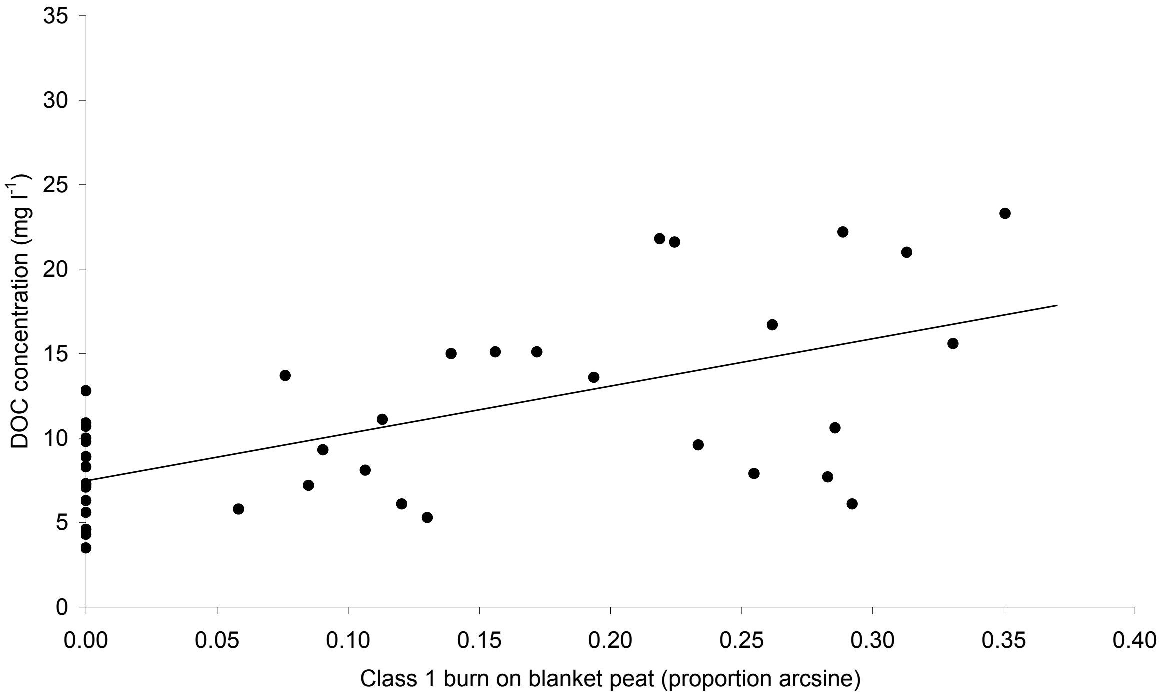


Figure 5.3.6. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for catchments sampled in March 2005 (r^2=0.38, p<0.001, n=42).

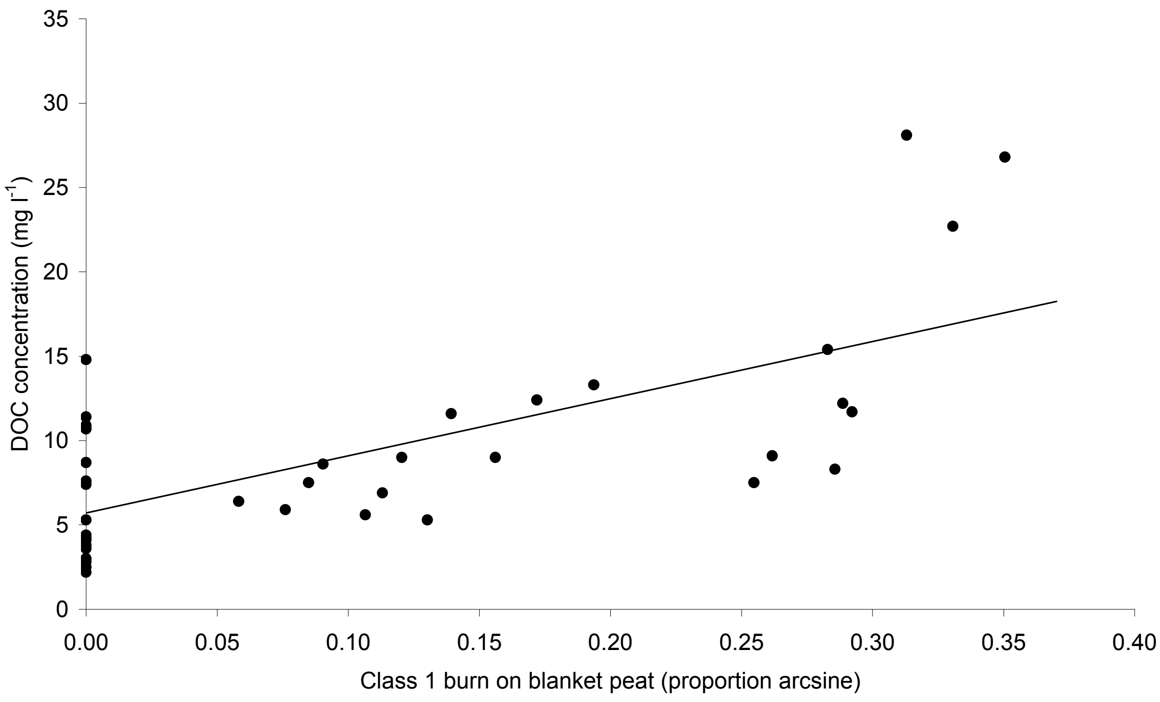


Figure 5.3.7. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for catchments sampled in January 2005 (r^2=0.45, p<0.001, n=39).

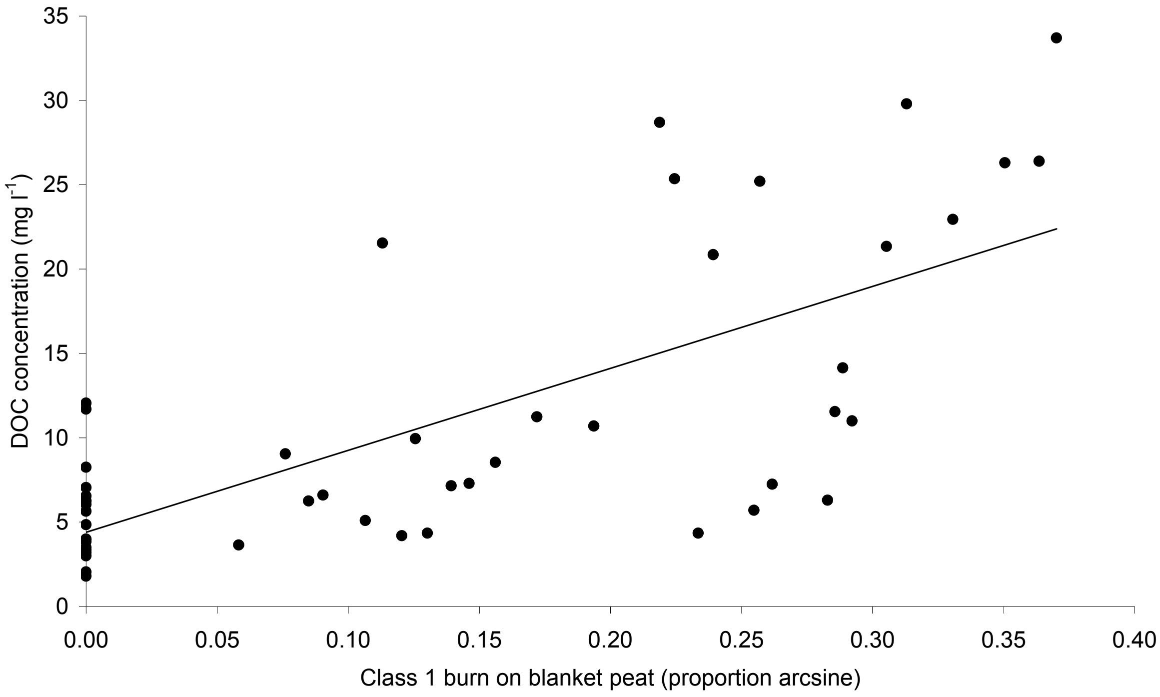


Figure 5.3.8. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for catchments sampled in November 2005 (r^2=0.51, p<0.001, n=50).

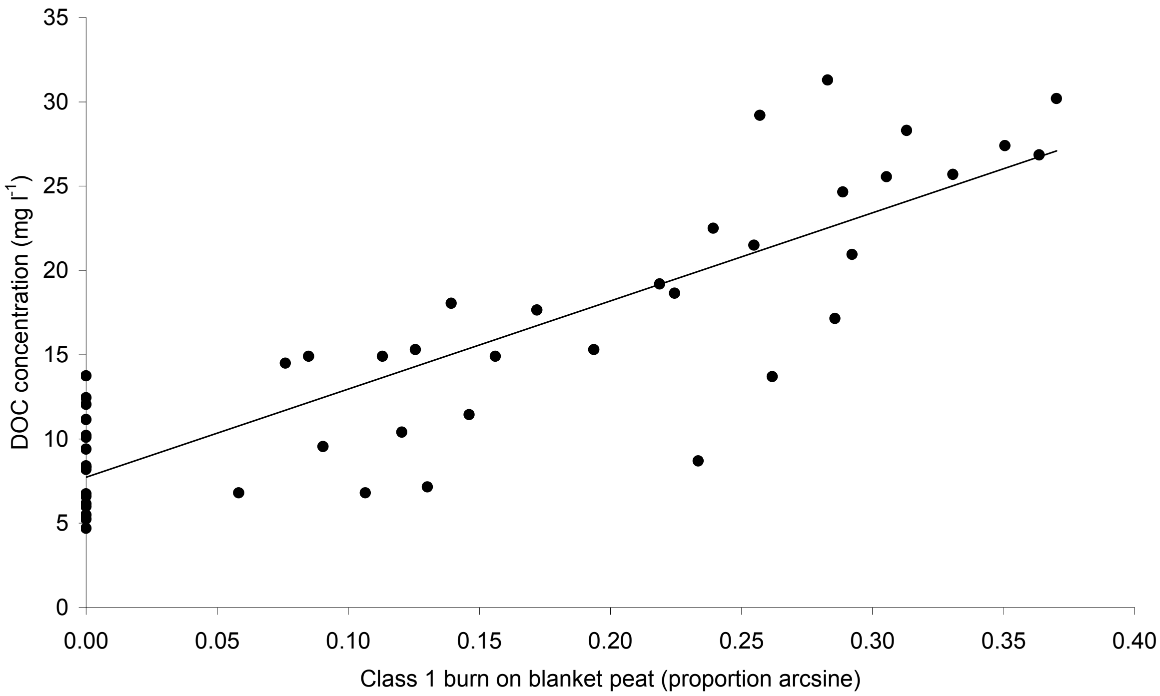


Figure 5.3.9. Proportion of catchment as Class 1 burn on blanket peat against DOC concentration for catchments sampled in December 2005 (r^2=0.74, p<0.001, n=50).

5.3.4. Blanket peat catchments

19 of the examined catchments contained in excess of 85% blanket peat. In catchments where samples were collected successfully in all four months (11), the only significant predictor of DOC concentration that entered into the regression was the proportion of new burn (Class 1) on blanket peat (r^2=0.50, *p*=0.009, Figure 5.3.10, Table 5.3.1). This relationship held in samples for all 19 catchments sampled in November and December, (r^2=0.46, *p*=0.001, Figure 5.3.11). There was no significant relationship between the remaining variation in proportion of peat and DOC.

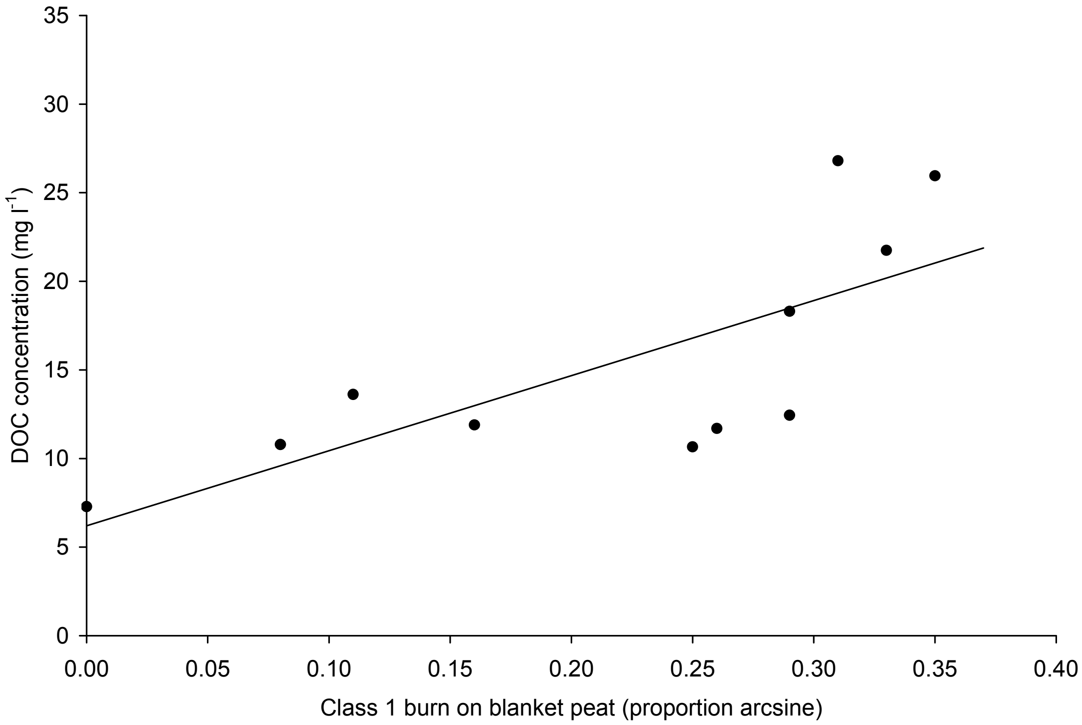


Figure 5.3.10. Proportion of catchment as Class 1 burn on blanket peat against four-month mean (Jan, Mar, Nov and Dec) DOC concentration for catchments containing at least 85% cover of blanket peat (r^2=0.50, *p*=0.009, n=11).

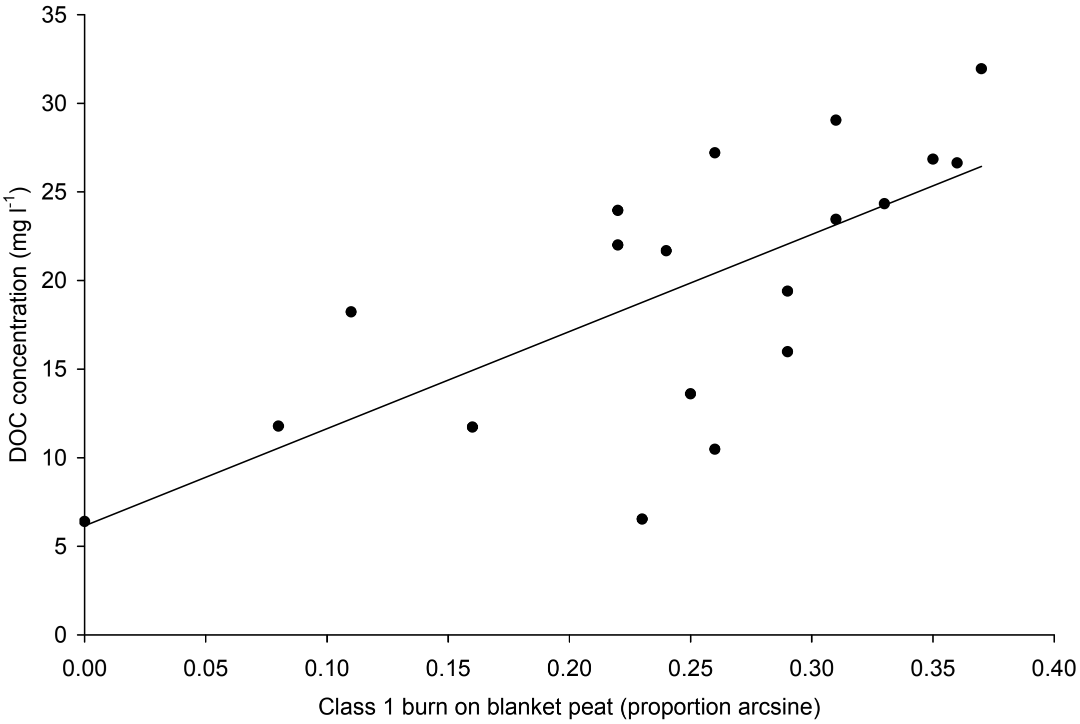


Figure 5.3.11. Proportion of catchment as Class 1 burn on blanket peat against two-month mean (Nov and Dec) DOC concentration for catchments containing at least 85% cover of blanket peat (r^2=0.46, p=0.001, n=19).

5.3.5. Removal of gripped catchments

For the catchments containing no artificial drainage (13 catchments containing visible evidence of gripping excluded), the proportion of new burn (Class 1) was again the only predictor of DOC concentration (Table 5.3.2) with r^2=0.64 (four-month mean) and r^2=0.70 (two-month mean). Analysis of covariance between gripped and non-gripped catchments identified no significant difference in either the slope or elevation between the two regression models (Figure 5.3.12).

Table 5.3.2. Exclusion of gripped catchments from analysis.

DOC measurement	Visibly gripped catchments included			Visibly gripped catchments excluded			ANCOVA - gripped and non-gripped	
	n	Predictor	r^2	n	Predictor	r^2	t (slope)	t (elevation)
4 month mean	39	Burn Cl1 on blanket peat	0.62 ***	29	Burn Cl1 on blanket peat	0.64 ***	0.38 †	0.41 †
2 month mean	50	Burn Cl1 on blanket peat	0.69 ***	37	Burn Cl1 on blanket peat	0.70 ***	0.56 †	1.29 †

***p<0.001; † not significantly different

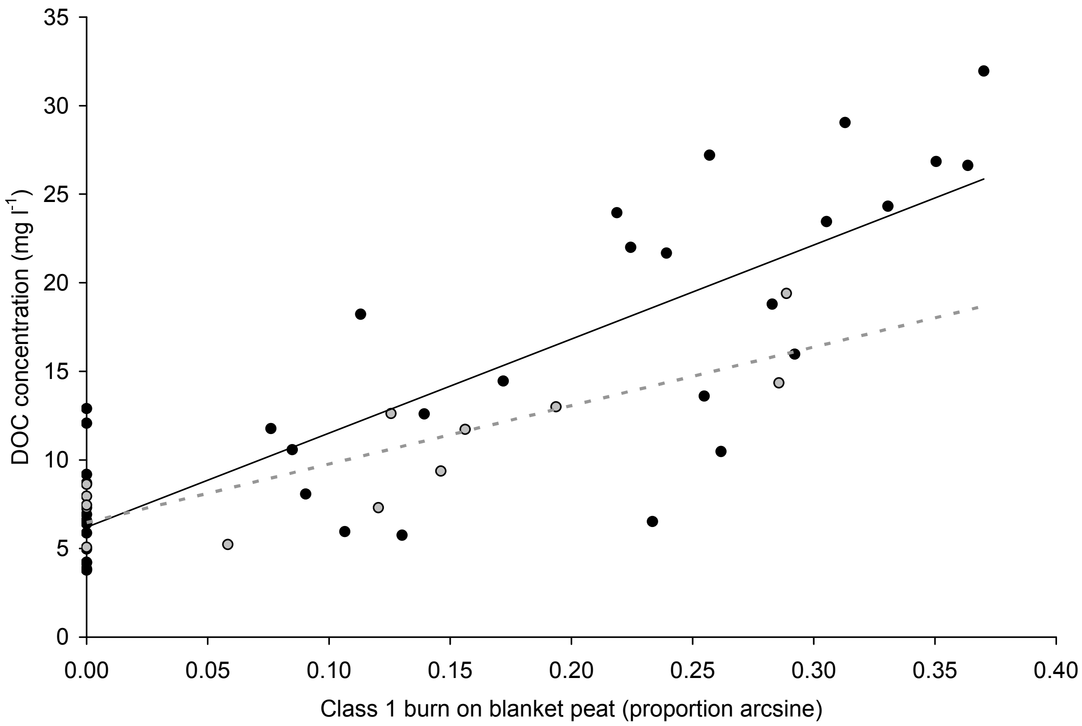


Figure 5.3.12. Proportion of catchment as Class 1 burn on blanket peat against two-month mean (Nov and Dec) DOC concentration for gripped (dashed) and non-gripped (solid) catchments. No significant difference in slope (t=0.56) or elevation (t=1.29).

5.3.6. Influence of catchments studied by Yallop *et al.* (2008)

Yallop *et al.* (2008) identified a relationship between the proportion of new burn on blanket peat and drainage water colour for 13 catchments in the South Pennines. As ten of these catchments are included in this study, the potential influence of these catchments on the results here was examined. By excluding the ten catchments previously studied by Yallop *et al.* (2008), the relationship between new burn and DOC concentration held in the remaining 40 catchments, with again the only predictor of DOC concentration identified as the proportion of new burn (Class 1) on blanket peat in both four-month mean (r^2=0.46) and two-month mean (r^2=0.67) analyses (Table 5.3.3). Analysis of covariance between the two groups of catchments identified no significant difference in either the slope or elevation between the two regression models (Figure 5.3.13).

Table 5.3.3. Exclusion of catchments examined by Yallop *et al*. (2008) from analysis.

	Yallop *et al*. (2008) catchments included			Yallop *et al*. (2008) catchments excluded			ANCOVA	
DOC measurement	n	Predictor	r^2	n	Predictor	r^2	t (slope)	t (elevation)
4 month mean	39	Burn Cl1 on blanket peat	0.62 ***	29	Burn Cl1 on blanket peat	0.46 ***	-1.03 †	-1.21 †
2 month mean	50	Burn Cl1 on blanket peat	0.69 ***	40	Burn Cl1 on blanket peat	0.67 ***	-0.19 †	-0.10 †

***p<0.001; † not significantly different

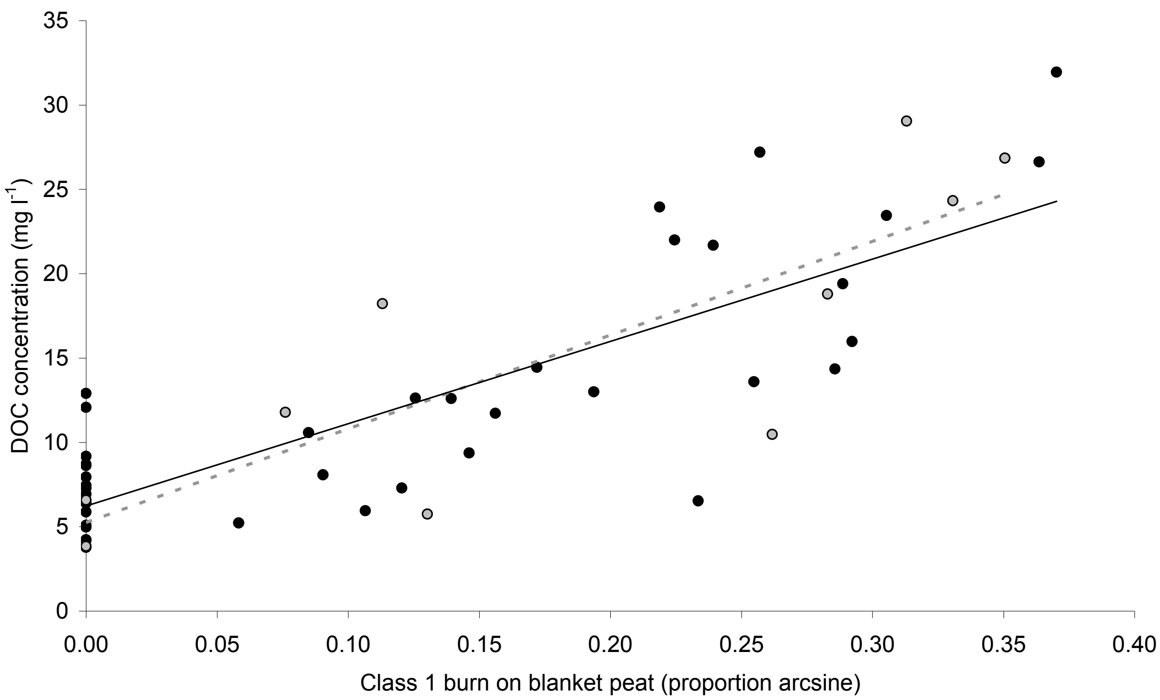


Figure 5.3.13. Proportion of catchment as Class 1 burn on blanket peat against two-month mean (Nov and Dec) DOC concentration for ten catchments studied by Yallop *et al*. (2008) (dashed) and the 40 remaining catchments examined in this study (solid). No significant difference in slope (t=-0.19) or elevation (t=-0.10).

5.3.7. Validity of analysis

Least squares regression analysis requires several conditions to be met for the test to be appropriate. The main conditions of linear regression (Fowler and Cohen, 1990) are:

i) there is a linear relationship between a dependent *y* variable and an independent *x* variable which is implied to be *functional* or *causal*;

ii) the *x* variable is not a random variable but is under the control of the observer;

iii) the data are normally distributed.

In the analysis conducted here, condition i) is met, as the relationship being examined is implied to be causal. Conditions ii) and iii) need to be considered during experimental design. Owing to the spatial constraints imposed upon the selection of catchments (Section 5.2.1), these two conditions were not ‘controlled’. However, the distribution of DOC concentration of samples collected in each month was tested using the Kolmogorov-Smirnov test in SPSS. The test identified that in November the distribution of DOC concentration was significantly different from a normal distribution ($p<0.05$) but in all other months, and combinations of months used in analysis, the data were not significantly different.

Further validation of whether the use of least squares regression is appropriate can be made if the variance of the residuals is homogenous across the range of predicted values (homoscedasticity). No formal test is available within SPSS; however, in general the residual variance appears homoscedastic, with the exception of the samples collected in January (Figure 5.3.7).

5.4. Discussion

Previous studies (e.g. McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001) have identified a positive relationship between the proportion of blanket or 'hill' peat in upland catchments and DOC concentration in the waters draining from them. Forced regression of the proportion of blanket peat (soil sub-group 1011b) against DOC concentrations for the catchments examined here also identified significant positive relationships, indicating the inevitable link between the size of the carbon pool within a catchment and the amount of DOC released (Hope *et al*., 1997a). However, this factor was not selected as the primary predictor of DOC in any of the multiple regression analyses undertaken here, and stronger relationships were consistently identified between the amount of new burn (Class 1) on blanket peat and DOC concentration (e.g. r^2=0.62 compared to r^2=0.37; Table 5.3.1), in three of the four regions examined (45 out of 50 catchments). These results suggest that the area of burn on blanket peat strongly influences the production and release of DOC from underlying soils. This is supported by the significant regression between area of new burn (Class 1) and DOC (r^2=0.46; p=0.001, 19 sample catchments) when data from only those catchments with greater than 85% blanket peat were examined in isolation, effectively removing the proportion of peat as a variable. That no significant differences in the burn-DOC relationship were identified between catchments containing visible evidence of gripping and those catchments that do not, suggests that the direct influence of drainage (at the density examined here) has little overall effect on DOC production and release.

The sampling regime for the study here was limited to four 'snapshots' of DOC concentration, and therefore does not encompass the full seasonal variation in production and release exhibited by catchments. However, changes in seasonal responses were identified, with the degree of variance explained by burning being higher for the November and December samples (r^2=0.51-0.74) compared to the January and March samples (r^2=0.38-0.45). This could be a result of the samples in November and December being collected earlier in the ‘flush’ period (e.g. Naden and McDonald, 1989) or due to fewer observations in January and March.

The interpretation that burning of vegetation on blanket peat enhances DOC release is supported by the observations that for three out of five cases where the regression model was improved significantly by inclusion of a second factor that exhibited a positive relationship to DOC concentration (Table 5.3.1), the factor selected was the proportion of recent burn (Class 2) on blanket peat. The other two cases of a second factor improving the model showed an inverse relationship to DOC. The inclusion of closed canopy *Calluna* on soils with peaty horizons for the catchments examined in South Yorkshire (Table 5.3.1) may arise as a consequence of the fact that as burning increases there is an inevitable concomitant decrease in area of older *Calluna* stands.

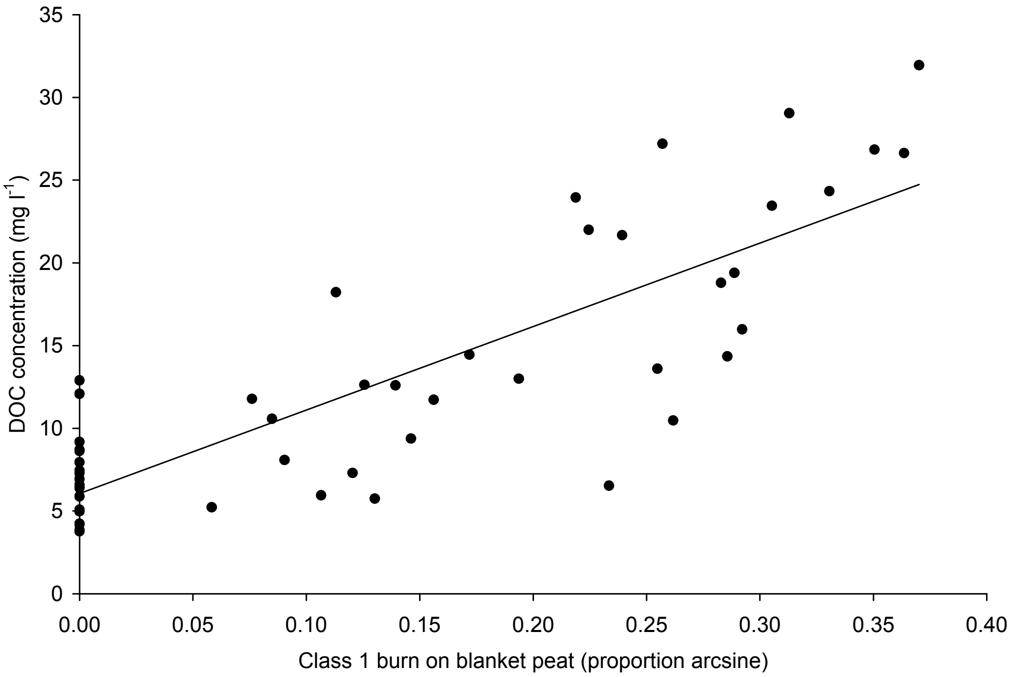
Although this relationship between area of new burn on blanket peat and DOC was only identified in three of the four regions, this arises simply because none of the five catchments examined in the North Yorkshire Moors region contained any coverage of blanket peat, although soils with peaty horizons are present. The soil groups in these catchments therefore have less potential for producing colour or DOC (McDonald *et al.*, 1991). This interpretation is supported both by the very low concentrations of DOC measured at these sites (Table 5.2.3), and because no significant predictor of DOC concentration was identified for this group of catchments. This also indicates that the main source of DOC to waters draining the upland catchments examined here is blanket peat, and is consistent with other observations (e.g. McDonald *et al*., 1991).

It is possible that the measurement of new burn area might simply be serving as a surrogate measurement of a <0.45 μm fraction of char or ash resulting from the burning of vegetation that is subsequently leached from the peat (Allen, 1964) and identified here as DOC. However there are two threads of evidence against this suggestion. The total area of new burn on all soil types was included in the multiple regression analyses, but was not identified as a significant predictor, as would be expected if the ash were contributing to DOC as this would source from all soil types. Secondly, the failure to identify a significant predictor of DOC concentration for catchments containing no cover of blanket peat suggests that the dominant form of DOC identified here is humic substances.

It is worthy of note that both DOC concentration and water colour were measured for all water samples collected (see Chapter 6.2.2), but DOC concentration was used in the analysis presented here as it is the metric most commonly used in other contemporary studies (e.g. Freeman *et al*., 2001; Evans *et al*., 2006; Monteith *et al*., 2007). Interestingly, if water colour, determined as Hazen, is used in analysis in place of DOC concentration, a higher degree of variance in water colour is explained by the proportion of Class 1 burn on blanket peat (e.g. r^2=0.76 compared to r^2=0.69; Figure 5.4.1). For catchments where the proportion of burning on blanket peat is zero (x=0), there is also a lower degree of variance in water colour, and this may indicate that not all the DOC measured is comprised of humic substances. The source of DOC measured for the samples collected in this study will be examined further in Chapters

6 and 8, and any implication this has on other studies focussing on the importance of DOC derived from peat will be discussed further in Chapter 9.

a)



b)

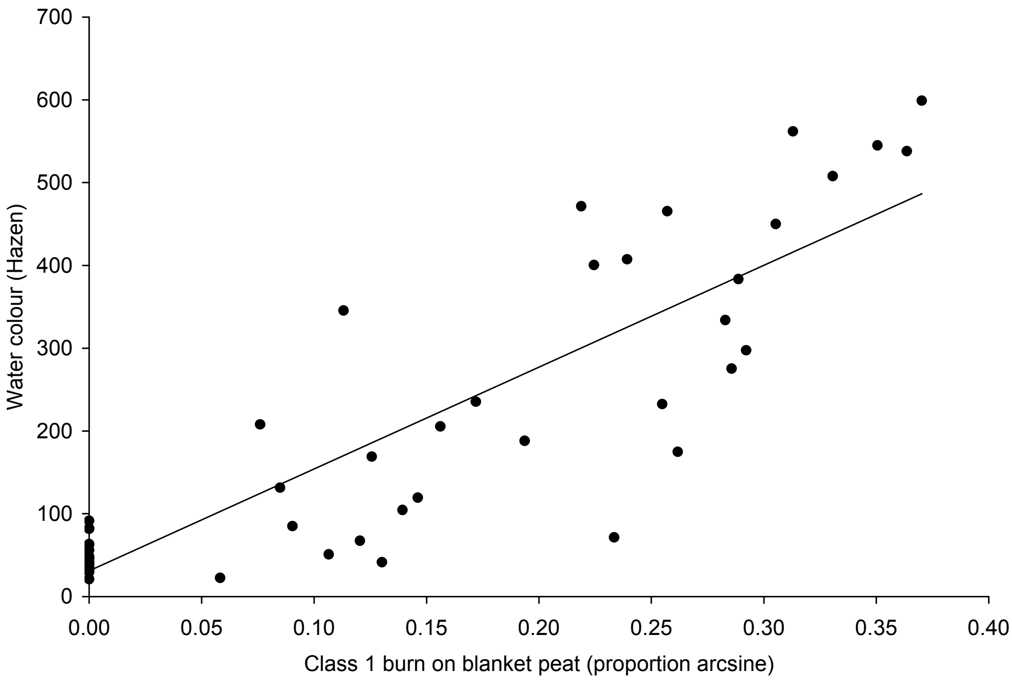


Figure 5.4.1. Proportion of catchment as Class 1 burn on blanket peat against two-month mean (Nov & Dec): a) DOC concentration (r^2=0.69, p<0.001; b) Hazen (r^2=0.76, p<0.001, n=50).

The strong relationship identified between the proportion of new burn on blanket peat and DOC concentration here is consistent with the observation of Yallop *et al*. (2008), who found that the proportion of new burn on deep peat explained 82% of the variance in water colour for the year 2000. That no significant difference was identified between the regression models for the ten catchments examined within that study, and the remaining 40 catchments examined here demonstrates that the catchments examined previously by Yallop *et al*. (2008) are not atypical in the South Pennines, but part of a widespread response in the area.

Although the evidence presented here would appear convincing, it is at variance with other studies that have identified no relationship between controlled burning and DOC concentrations. Ward *et al*. (2007) showed no difference in interstitial DOC concentration in peat under burns in well-managed rotations (i.e. burned every ten years), and Worrall *et al*. (2007) found DOC concentrations to be lower under those circumstances. While this might be considered contrary to the results here, it should be noted that both of these studies relate to burns that had already recovered to full canopy. These correspond to Class 3 and Class 4 burns as described here, and in this study no such relationship was observable either, implying that the phenomenon of enhanced DOC release as a consequence of fire management is time-limited to a period of less than ten years. Clay *et al*. (2009) monitored DOC concentration in interstitial and surface water runoff for the year following a controlled ‘cool’ burn, but found no significant difference in DOC concentration in either interstitial or surface water. However, it must be noted that Clay *et al*. (2009) did not measure DOC concentration in drainage water as examined here.

The effect of controlled burning on DOC concentration in catchment drainage has, however, also been examined by O'Brien *et al*. (2008), where burning management was ceased in a study catchment and drainage DOC compared to control catchments over a period of 3-4 years. No significant difference in DOC concentration was found over the period of study, although the authors note that longer term study may be required to detect any change as a result of management manipulation. This suggestion is supported by the observation that 'new' burns, with which the relationship with drainage DOC was identified here, are visible in aerial photography for more than four years (Chapter 4.3.4).

5.5. Conclusion

The percent cover of blanket peat in a catchment was found to be significantly related to DOC concentration in drainage waters for 50 small headwater catchments examined in the South Pennines and on the North Yorkshire Moors. However, the area of new vegetation burn on blanket peat was consistently shown to be the most significant predictor of drainage DOC concentration and indicates that such form of management can influence the production and release of DOC from underlying soils. The effect of fire management on drainage DOC concentration was detected for 50 catchments smaller than 3 km^2. Considering the observed increases in DOC concentration in surface waters in the UK and the challenges facing water utility companies to meet legislative standards for potable water supply, there is a need to understand whether the effects of fire management identified here are significant at larger geographic scales. This could have consequence for the water supply industry in terms of catchment management and will be examined in Chapter 6.

Chapter 6 – Spatial variation in DOC production and release from upland peat soils II: reservoir catchments

6.1. Introduction

The treatment of water colour is an increasing problem for water utilities to meet legislative standards of potable water supply, a key ecosystem service provided by upland areas. The consistent identification of a relationship between the proportion of new burn on blanket peat within a catchment and DOC concentration in drainage water for the 50 small headwater catchments examined in the South Pennines and on the NYM in Chapter 5, could indicate a potential link with current high levels of water colour observed in upland reservoirs (Watts *et al.*, 2001). However, the catchments examined in Chapter 5 individually cover an area less than 3 km^2, and the significance of peat soils in determining DOC concentrations in drainage has been found to decrease with catchment size (Aitkenhead *et al.*, 1999). In larger-scale catchments other factors including agriculture and forestry (Eckhardt and Moore, 1990) may become more important. The automatic extrapolation of the effects of the factors shown to influence DOC production in soils within catchments smaller than 3 km^2 to DOC concentrations in drainage for larger scale catchments, and consequently of importance to the water supply industry, is therefore not straightforward and requires further examination. If the effects of fire management on DOC production in blanket peat are detectable in drainage for larger scale catchments, this could have benefit for water utilities in promoting altered catchment management to land owners.

There is little monitoring of DOC concentrations in surface waters at this scale, however, UK water utility companies that source reservoir water from upland peat catchments frequently monitor water quality parameters, including water colour, at a number of water treatment works (WTWs). Water colour, as it primarily arises from humic and fulvic acids (Aiken *et al*., 1985), can serve as a proxy for DOC concentration (Kerekes *et al*., 1986; Eatherall *et al*., 1998; Worrall *et al*., 2003). Water utility colour data also have several advantages over short-term sampling as undertaken in Chapter 5. These data provide a greater number of measurements of DOC over the course of a year and water colour of reservoir outflow is greatly buffered compared to inlet colour (Pattinson *et al*., 1994) thereby reducing potential short-term effects from external factors such as precipitation on colour or DOC concentrations (Grieve, 1984).

The aim of this chapter is to examine land use within geographically defined reservoir catchments and determine whether any relationships exist between these and drainage DOC concentration. The objectives defined to undertake this were:

i. select a series of upland catchments, located in the same study area as the catchments examined in Chapter 5, for which water quality data are available;
ii. examine the relationship between water colour and DOC to allow estimation of DOC concentration for each selected catchment;
iii. source aerial imagery for years of colour data availability and derive land use/management statistics and physical catchment descriptors;
iv. identify any relationships between land use and DOC concentrations.

6.2. Methods

6.2.1. Reservoir catchment selection

To examine potential relationships between land use and DOC concentration in drainage waters, the true extent of the catchment area supplying water to a measured sample must firstly be accurately determined. Many WTWs are supplied by several reservoirs or conversely a single reservoir may supply more than one WTW. Further complications arise where water supplied to a WTW is sourced via linked reservoirs (i.e. where one reservoir is supplied by the outflow of another) or is supplemented by sporadic contribution pumped from streams via intake supplies. In such cases the fractional contribution of individual components in the supply chain to a measured sample cannot be determined without detailed operational data.

In total, water colour data were available for 29 WTWs in the South Pennines and NYM. GIS data containing the locations of WTWs and the spatial extents of all catchment areas supplying each WTW were sourced from the water utility company. Those with complex water supply chains were excluded and this left nine topographically defined reservoir catchments and their respective WTW data suitable for analysis (Figure 6.2.1; Table 6.2.1).

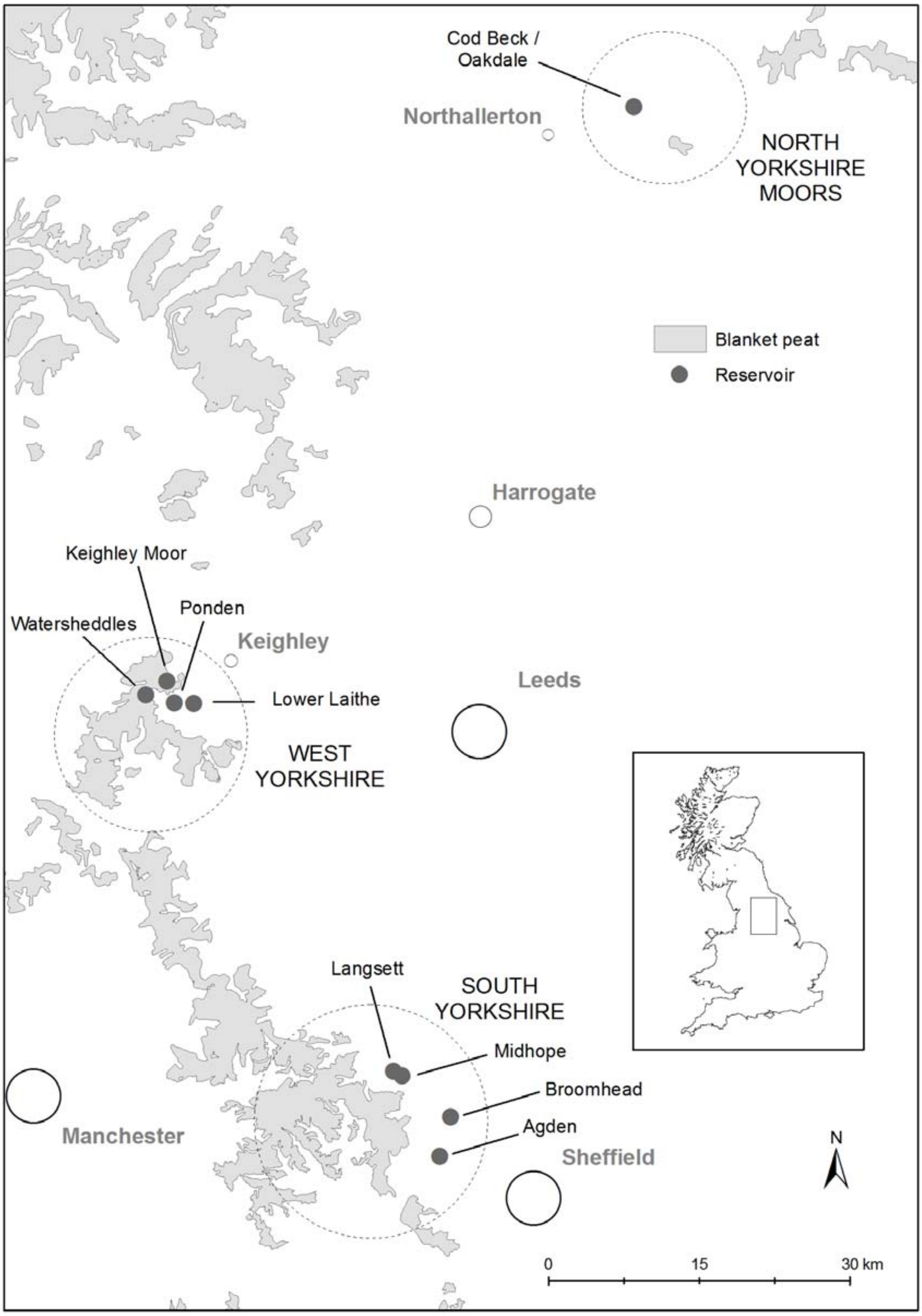


Figure 6.2.1. Location of reservoirs selected for analysis. Dotted circles indicate study areas examined in Chapter 5.

Table 6.2.1. Percent land use, vegetation, management and soil type combinations and DOC measurements used for catchments in analysis of land use and DOC.

Reservoir	WTW	Location	Area (km^2)	Mean slope (degrees)	Water colour data	
					1999	2005
Agden	Loxley	SY	12.2	8.4	All months	All months
Broomhead	Ewden	SY	21.4	8.5	All months	All months
Cod Beck/ Oakdale	Osmotherley	NYM	9.6	6.4	All months	All months
Keighley Moor	Oldfield *	WY	1.5	4.7	Jan - Aug	Jan-Apr, Jun, Sep
Langsett	Langsett *	SY	20.9	7.3	All months	All months
Lower Laith	Sladen Valley *	WY	5.0	7.8	All months	All months
Midhope	Langsett *	SY	4.2	7.3	All months	All months
Ponden	Sladen Valley *	WY	7.6	10.7	All months	All months
Watersheddles	Oldfield *	WY	2.7	6.7	All months	Jan-Apr, Jun, Sep

* where the same WTW is referenced for different reservoirs, water is sampled separately.

6.2.2. Relationship between water colour and DOC concentration

DOC concentration and water colour measured as Hazen (see Chapter 3.3) were determined for 181 water samples collected from the 50 catchments examined in Chapter 5. A number of the samples were collected from the headwaters in seven of the reservoir catchments examined here. The relationship between Hazen and DOC was determined using linear regression of Hazen against DOC for the 181 samples. Any seasonal variation in the colour-DOC relationship was also examined.

6.2.3. Derivation of DOC concentration

Water colour measurements as Hazen units were obtained for the nine selected reservoirs for calendar years 1999 and 2005, as aerial imagery was available for both these years (Section 6.2.4). Mean monthly colour was calculated for all months in each data record. Owing to breaks in the colour record at Keighley Moor and Watersheddles, colour data were only available for six months in 2005 (January, February, March, April, June and September) for these two reservoirs. There were further gaps in the colour record for Keighley Moor in 1999, where colour data were only available for January to August (Table 6.2.1).

Average water colour for each catchment was therefore determined for two time periods. For the year 1999, an eight month mean colour (January to August) was calculated for all nine reservoirs. An annual mean colour was also calculated for the eight catchments excluding Keighley Moor. For the year 2005, a six-month mean colour (Jan-Apr, Jun and Sep) was calculated for each of the nine reservoirs. An annual mean colour was also calculated for the seven reservoirs selected excluding Keighley Moor and Watersheddles.

Annual DOC concentration was then estimated for these mean colour values using the relationship between DOC concentration and Hazen determined in Section 6.2.2. As the peak in colour/DOC coincides with the division between water years, annual mean values determined in this analysis were based on the calendar year.

6.2.4. Land use/management and soil distribution

25cm resolution colour aerial photography for the nine reservoir catchments selected for analysis was obtained for the years 1999 and 2005. Land cover classes defined in Chapter 5.2.2 and an additional class for broadleaf woodland (as this occurred for the first time in this analysis) were mapped for each catchment using ArcGIS:

- unimproved grassland;
- semi-improved grassland;
- coniferous plantation;
- broadleaf woodland;
- ericaceous dominated (predominantly *Calluna*) moorland;
- grass/sedge dominated moorland.

Areas of vegetation burn Class 1 (new burn), Class 2 (recent burn) and Classes 3 and 4 (closed canopy heath) (see Chapter 3.2.2) were mapped within areas of *Calluna* dominated moorland.

Soils present within each reservoir catchment were identified by intersecting digital soil data with catchment boundaries. These were subsequently categorised into three broad soil types: blanket peat, upland soils with peaty horizons and non-peaty soils (Table 6.2.2), following the descriptions given by Avery (1980). The areal extent of all combinations of land use, management and soil type present in each catchment were then derived using ArcGIS and converted to proportions. Variables that occurred in only one catchment were excluded from analysis (Table 6.2.3).

Table 6.2.2. Soils present in reservoir catchments used in analysis, categorised into broad soil type following descriptions by Avery (1980).

Soil type	Blanket peat	Upland soils with peaty horizons	Non-peaty soils
Soil group	*Raw peat soils*	*Stagnopodzols*	*Non-calcareous pelosols*
Soil sub-groups	1011b	651a; 652	421a
		Stagnohumic gley soils	*Brown earths*
		721b, c	541f, g, y
			Podzols
			631a
			Stagnogley soils
			711p; 712a; 713g

Table 6.2.3. Land use and management variables by soil type (percent of catchment shown). CL1: Class 1 burn; CL2: Class 2 burn; CC: Closed canopy heath; CM: *Calluna* moorland; GM. Grass/sedge moorland; BW: Broadleaf woodland; IG: Improved grassland; PL: Plantation; UG: Unimproved grassland.

	Soil type			Blanket Peat (BP)					Upland peat soils (PH)								Non peaty soils (NP)				DOC (mg l^{-1})	
Reservoir	BP	PH	NP	CL1	CL2	CC	CM	GM	BW	CL1	CL2	CC	CM	IG	PL	GM	BW	IG	PL	UG	Monthly mean	Annual mean
1999																					8 month	
Agden	34	56	8	6	2	22	31	3	5	5	1	12	19	9	3	19	0	5	2	2	7.17	7.33
Broomhead	42	41	14	6	7	25	37	5	4	3	2	8	12	7	7	10	2	8	1	2	9.40	9.61
Cod Beck/Oakdale	0	88	11	0	0	0	0	0	0	8	7	45	61	3	6	18	0	3	3	4	5.49	5.37
Keighley Moor	96	0	0	4	2	61	67	28	0	0	0	0	0	0	0	0	0	0	0	0	7.34	†
Langsett	51	40	6	6	6	24	37	14	0	5	3	8	15	3	4	18	0	3	0	0	9.60	9.80
Lower Laithe	22	58	17	0	0	8	8	14	0	4	3	27	34	3	0	21	1	14	1	1	6.12	6.11
Midhope	36	55	3	3	4	15	22	14	0	10	5	10	25	11	8	11	0	1	1	1	5.70	5.67
Ponden	50	42	7	2	3	27	32	17	0	1	0	5	6	23	0	13	0	7	0	0	7.52	7.52
Watersheddles	83	13	0	7	5	29	40	42	0	0	0	0	2	0	0	10	0	0	0	0	9.73	9.59
2005																					6 month	
Agden	34	56	8	7	12	13	32	2	6	3	7	8	18	9	3	19	0	5	2	2	8.36	8.29
Broomhead	42	41	14	13	8	16	37	5	4	4	4	5	13	7	7	9	2	8	1	2	10.40	10.56
Cod Beck/Oakdale	0	88	11	0	0	0	0	0	0	13	28	19	60	3	6	19	0	3	3	4	5.69	5.77
Keighley Moor	96	0	0	8	5	56	68	27	0	0	0	0	0	0	0	0	0	0	0	0	9.52	†
Langsett	51	40	6	7	7	26	40	11	0	5	4	9	17	3	4	16	0	3	3	0	10.17	10.57
Lower Laithe	22	58	17	0	0	8	8	14	0	1	4	27	32	3	0	22	1	14	1	1	6.02	6.19
Midhope	36	55	3	6	5	12	23	13	0	7	12	7	26	11	8	10	0	1	1	1	6.09	6.15
Ponden	50	42	7	3	2	26	32	18	0	0	1	4	5	24	0	13	0	7	0	0	6.92	7.31
Watersheddles	83	13	0	7	7	27	40	42	0	0	0	0	2	0	0	10	0	0	0	0	9.75	†

† Incomplete data record – not calculated. Excluded from analysis.

6.2.5. Statistical analysis

Owing to missing colour data from Keighley Moor and Watersheddles, two separate analyses were undertaken for each year of data availability. Firstly data from all nine catchments were used with mean DOC concentration calculated from the six or eight months available for all catchments. Secondly the seven or eight catchments with complete annual records were analysed using a mean annual DOC measurement. In all cases relationships between land use/management and DOC concentration in associated drainage water were examined using stepwise multiple regression. Mean catchment slope and all land use/management/soil type variables (Table 6.2.2) were regressed against the calculated mean DOC concentrations. To increase the number of observations, a final analysis was performed using all annual mean DOC concentrations in both years for the catchments available. Variables were normalised prior to regression analysis using the arcsine-square root transformation (Fowler and Cohen, 1990). Analysis was undertaken using SPSS version 15.0.

6.3. Results

6.3.1. Relationship between Hazen and DOC concentration

A highly significant (p<0.001) positive relationship was identified between Hazen and DOC concentration for the 181 samples assessed (r^2=0.93; Figure 6.3.1; Equation 6.3.1). Analysis of covariance identified no significant difference between the regression models determined for individual months (Table 6.3.1), indicating that seasonal variation in the Hazen-DOC relationship for the catchments examined is minor in the months examined.

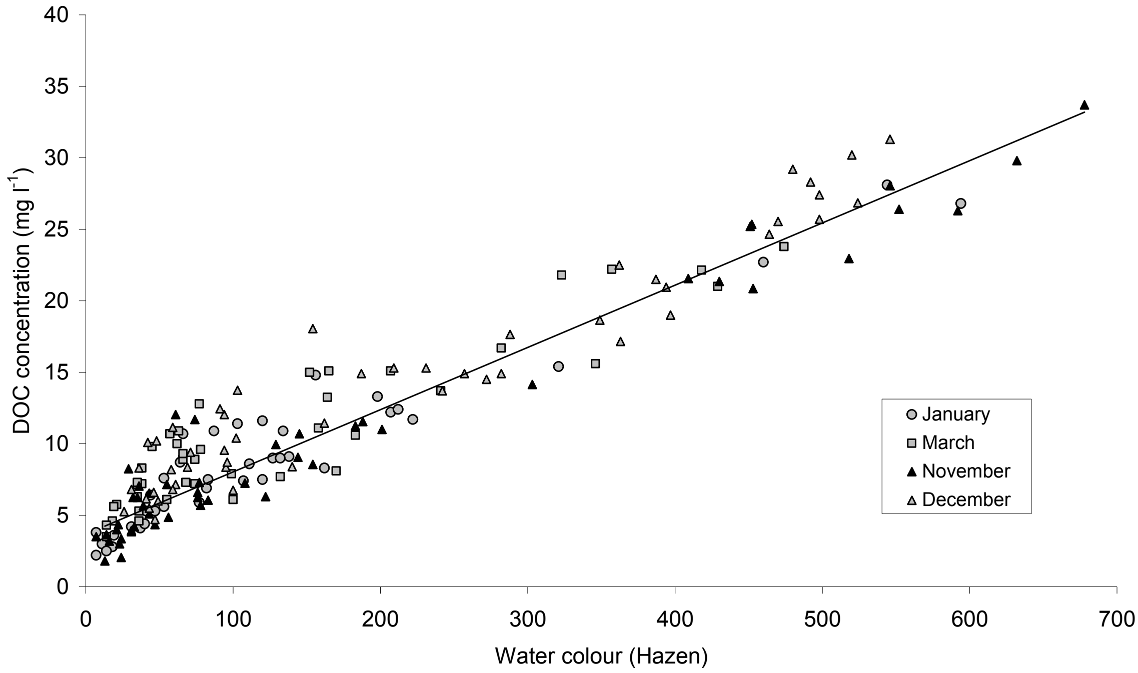


Figure 6.3.1. Relationship between water colour (Hazen) and DOC concentration in drainage for 50 catchments sampled in 2005 (r^2=0.93, p<0.001; n=181).

$$\text{DOC concentration} = 0.044 * \text{Hazen} + 3.89 \qquad (6.3.1)$$

Table 6.3.1. Variation in water colour-DOC relationship for 50 catchments sampled in 2005.

	Hazen-DOC regression equation (± s.e.)	r^2	n	ANCOVA (t) slope	ANCOVA (t) elevation
All samples	DOC = 0.044 * Hazen + 3.89 (±2.14)	0.93 ***	181		
January	DOC = 0.042 * Hazen + 3.88 (±1.78)	0.91 ***	39	0.07 n.s.	1.05 n.s.
March	DOC = 0.040 * Hazen + 4.40 (±2.13)	0.86 ***	42	0.19 n.s.	-1.85 n.s.
November	DOC = 0.042 * Hazen + 3.54 (±1.82)	0.96 ***	50	0.05 n.s.	1.73 n.s.
December	DOC = 0.043 * Hazen + 4.47 (±2.15)	0.93 ***	50	0.02 n.s.	-1.95 n.s.

*** p<0.001, n.s. not significant

6.3.2. Relationships between land use and DOC

1999

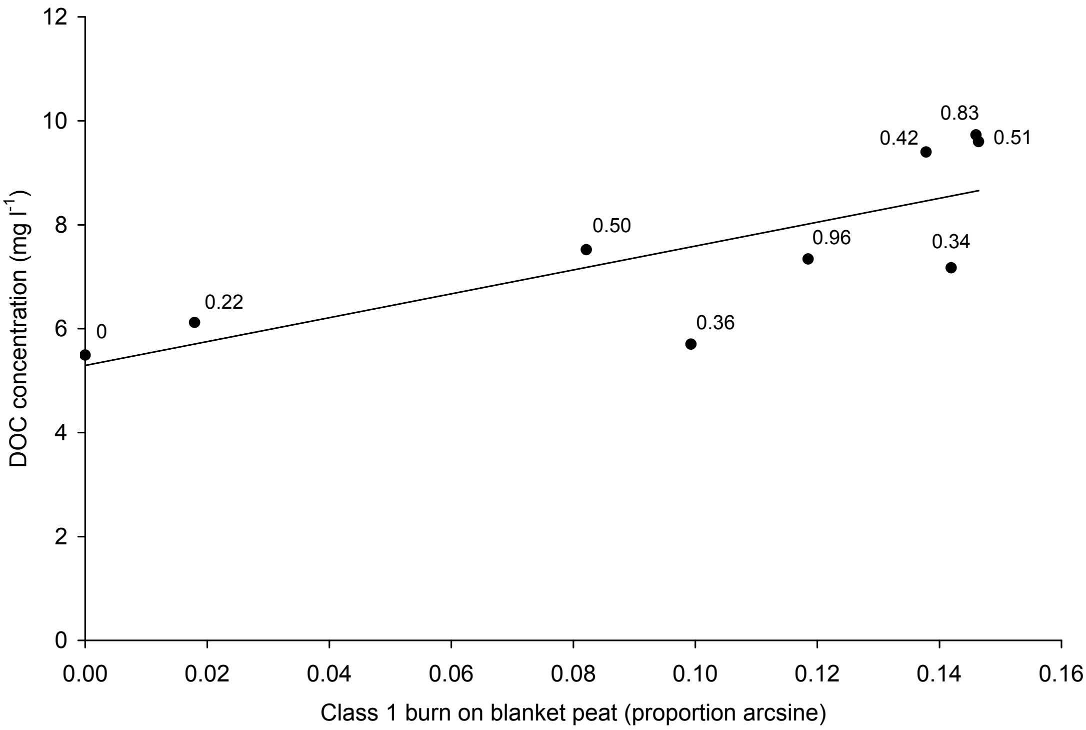
For the nine catchments examined using eight month mean DOC concentration, the only factor selected by the forward-entry multiple regression was the proportion of new burn (Class 1) on blanket peat. The relationship was significant (p=0.016) where burning on blanket peat explains 59% of the variance in DOC concentration between catchments (Table 6.3.2; Figure 6.3.2a). The relationship held when annual mean DOC was tested and again new burn on blanket peat was the only factor entered into regression for the eight catchments examined (r^2=0.63, p=0.018; Figure 6.3.2b). Forced regression of the proportion of blanket peat against DOC was significant only when tested using annual mean DOC (r^2=0.48, p=0.034).

Table 6.3.2. Predictors of DOC concentration identified using forward entry multiple regression, condition of entry = p<0.05.

Analysis	n	Primary predictor ¥	r^2	p	Regression model	Blanket peat †	p
1999							
8 month mean	9	Burn Cl 1 on blanket peat	0.59	0.016	DOC = 23.0 * Cl1 + 5.30	0.22	n.s.
Annual mean	8	Burn Cl 1 on blanket peat	0.63	0.018	DOC = 23.8 * Cl1 + 5.23	0.48	0.034
2005							
6 month mean	9	Burn Cl 1 on blanket peat	0.64	0.010	DOC = 22.0 * Cl1 + 5.41	0.37	0.048
Annual mean	7	Burn Cl 1 on blanket peat	0.60	0.023	DOC = 21.2 * Cl1 + 5.58	0.34	n.s.
1999 & 2005							
Annual mean	15	Burn Cl 1 on blanket peat	0.61	0.001	DOC = 22.0 * Cl1 + 5.44	0.18	n.s.

¥ no second variable entered into regression
† result from single linear regression

a)



b)

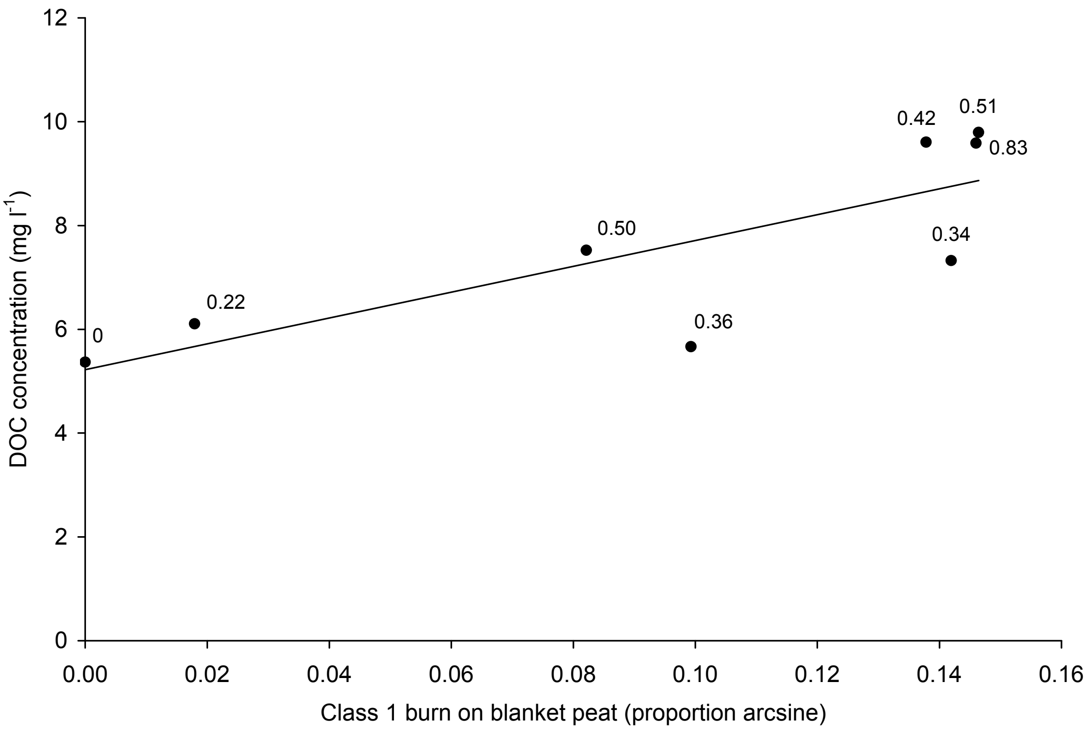
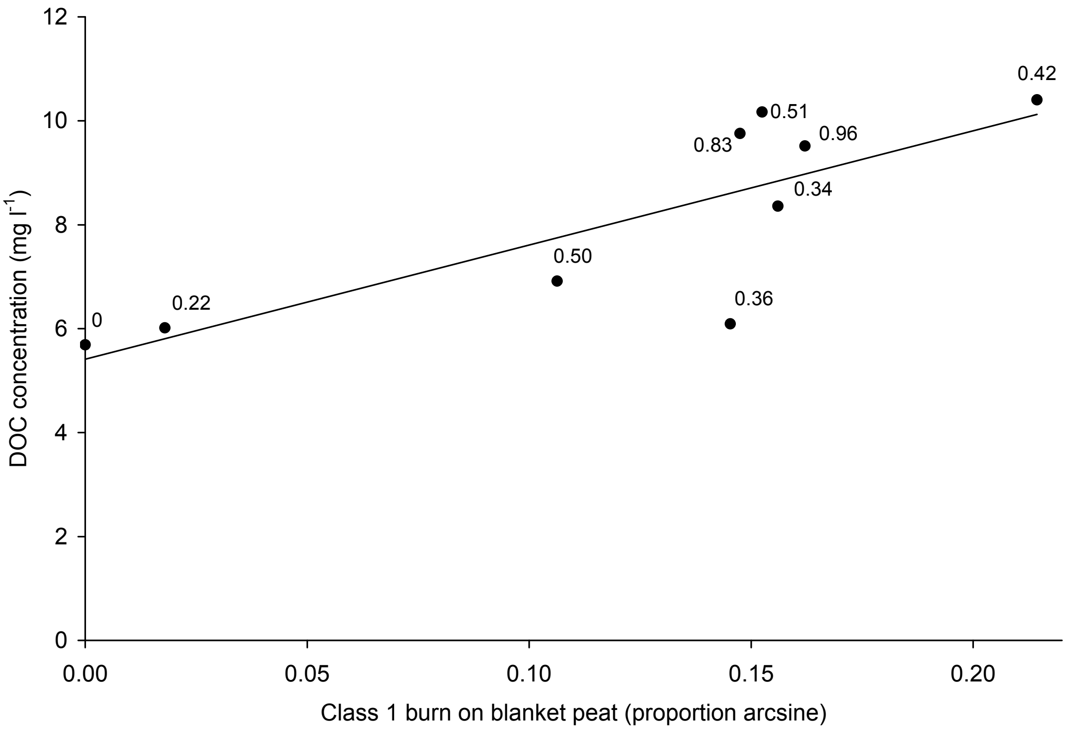


Figure 6.3.2. Proportion of catchment as Class 1 burn on blanket peat against mean DOC concentration for reservoir catchments in 1999. a) eight month mean DOC (r^2=0.59, *p*=0.016, n=9); b) annual mean DOC (r^2=0.63, *p*=0.018, n=8). Non-transformed proportion of catchment covered by blanket peat labelled.

2005

For both mean DOC concentrations examined in 2005, the proportion of Class 1 (new burn) on blanket peat was again the only factor selected in forward-entry multiple regression. For the nine catchments examined using six month mean DOC concentration, burning on blanket peat explains 64% of the variance in DOC concentration (p=0.01; Figure 6.3.3a). For the seven catchments examined using annual mean concentration, burning on blanket peat explains 60% of the variance in DOC concentration (p=0.023; Figure 6.3.3b). Forced regression of the proportion of blanket peat against DOC was significant only when tested using eight month mean DOC concentration (r^2=0.37, p=0.048).

a)



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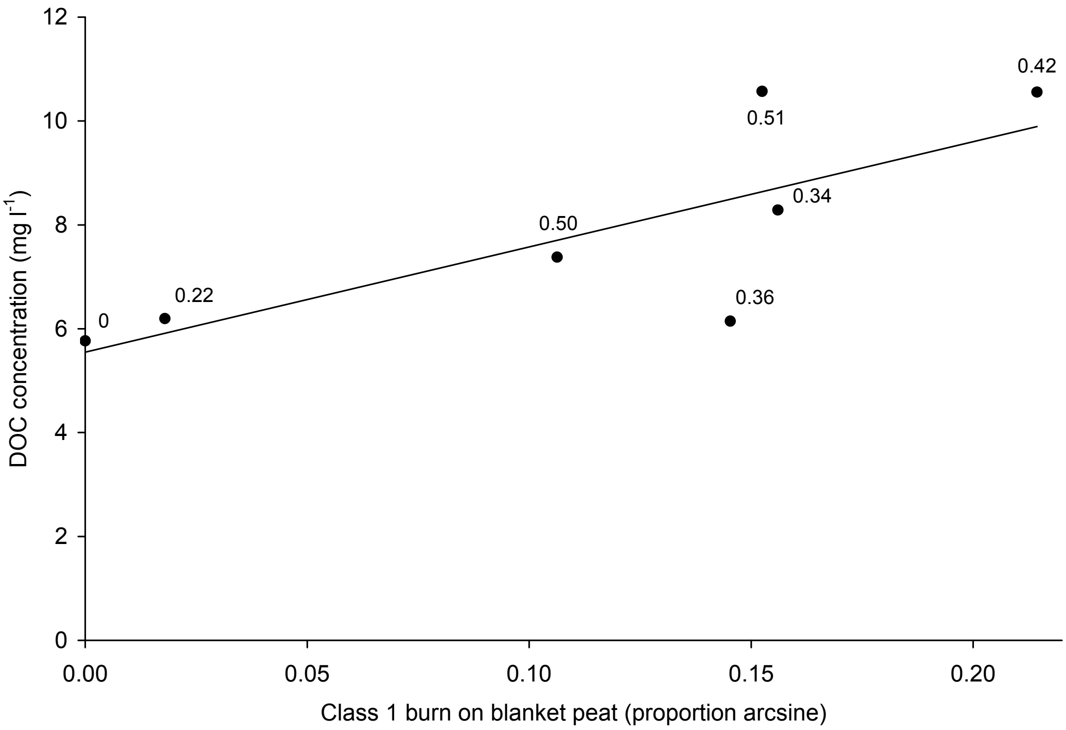


Figure 6.3.3. Proportion of catchment as Class 1 burn on blanket peat against mean DOC concentration for reservoir catchments in 2005. a) six month mean DOC (r^2=0.64, p=0.01, n=9); b) annual mean DOC (r^2=0.60, p=0.023, n=7). Non-transformed proportion of catchment covered by blanket peat labelled.

1999 and 2005

With the increased number of observations of land use and annual mean DOC available for eight catchments for 1999 and 2005, the only factor entered into multiple regression was again the proportion of new burn on blanket peat. The new burn-DOC relationship identified was highly significant (r^2=0.61, *p*=0.001; Figure 6.3.4). Figure 6.3.5 illustrates the changes in mean DOC concentration and proportion of new burn by catchment between the years 1999 and 2005. For Lower Laithe and Cod Beck/Oakdale catchments, where no change in the area of new burn on blanket peat was determined, and for Watersheddles catchment where the change in area of burn determined was less than 1% of the catchment (0.1 ha), DOC concentrations changed by between 0.02-0.2 mg l^{-1} (Table 6.2.3). For the remaining six catchments, where changes in the area of new burn were determined to be at least 1% of the catchment, the changes in DOC ranged from 0.39-2.18 mg l^{-1}. Midhope catchment fell below the regession model for both years.

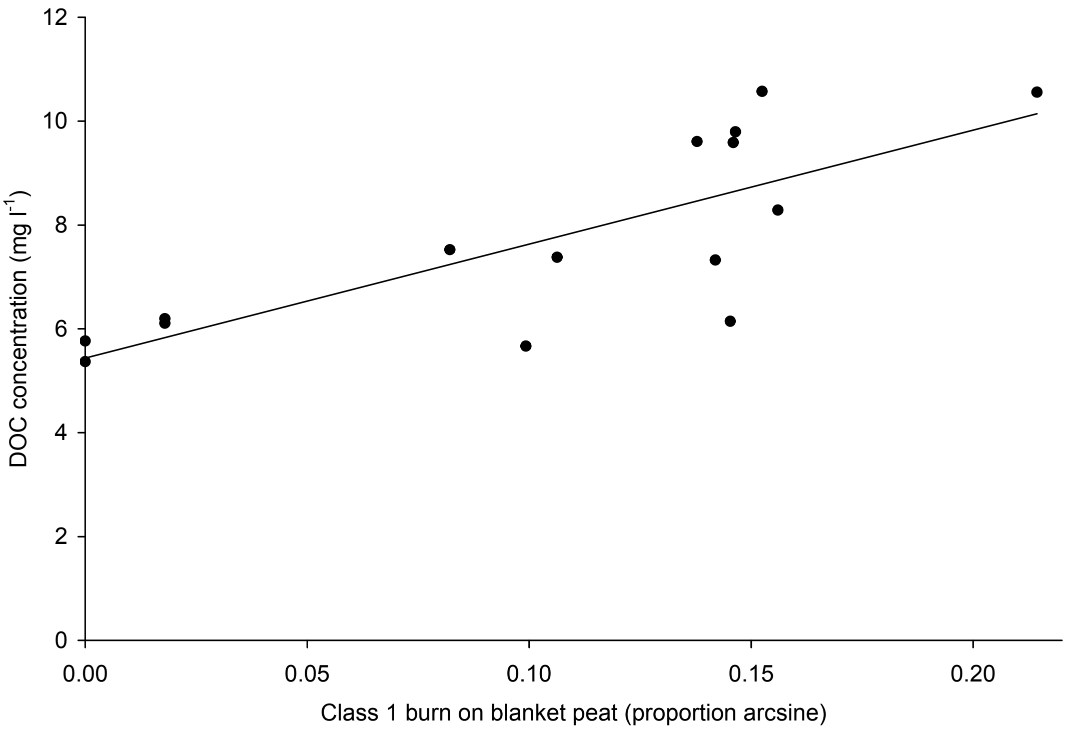


Figure 6.3.4. Proportion of catchment as Class 1 burn on blanket peat against mean DOC concentration for eight reservoir catchments in 1999 and seven catchments in 2005 (r^2=0.61, p=0.001, n=15).

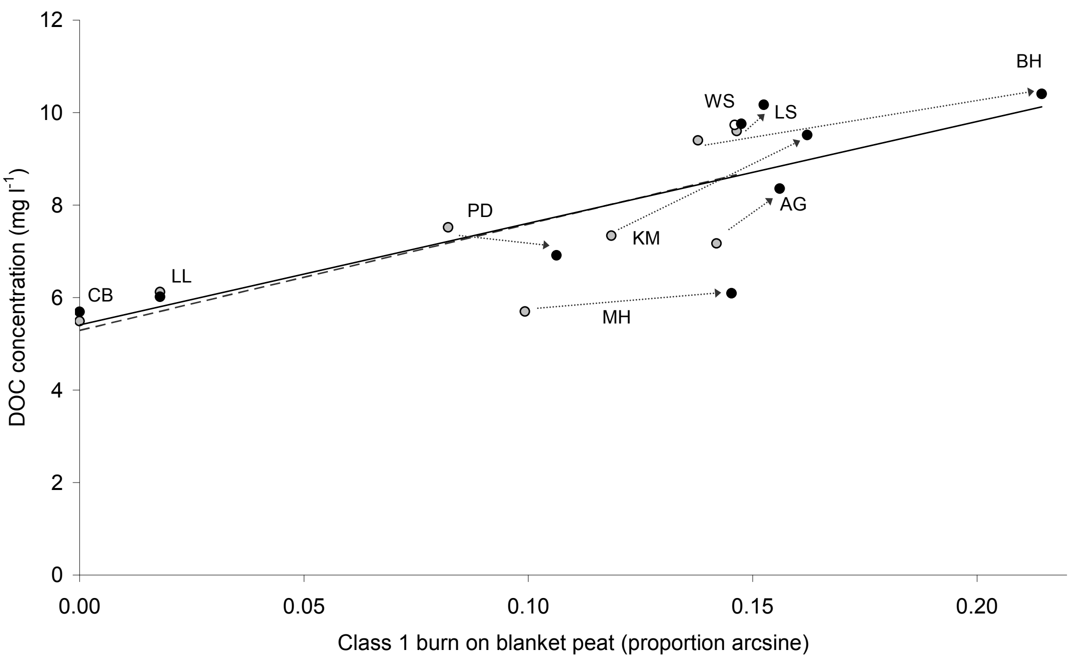


Figure 6.3.5. Proportion of catchment as Class 1 burn on blanket peat against mean DOC concentration for nine reservoir catchments (grey- eight month mean DOC for 1999; black – six month mean DOC for 2005; Watersheddles catchment for 1999 shown as open circle for clarity). AG – Agden; BH – Broomhead; CB – Cod Beck/Oakdale; KM – Keighley Moor; LS – Langsett; LL – Lower Laithe; MH – Midhope; PD – Ponden; WS – Watersheddles.

6.4. Discussion

A highly significant linear relationship was identified between Hazen and DOC concentration for 181 samples taken from 50 upland peat catchments (Chapter 5) in the South Pennines and NYM in 2005 (Figure 6.3.1). This suggests that WTW colour monitoring can provide a surrogate for DOC where the measured DOC arises primarily from humic substances. This relationship was therefore used to estimate DOC concentration from Hazen measured for water sampled from eight reservoirs in the South Pennines and one reservoir in the NYM in 2005. This water colour-DOC relationship has been used previously (Kerekes *et al*., 1986; Eatherall *et al*., 1998; Worrall *et al*., 2003), and the relationship determined for water sampled from the study areas examined here (Equation 6.3.1) is close to that derived for the River Tees in England by Worrall *et al*. (2003a) (Equation 6.4.1). The relationship derived from waters sampled in western Nova Scotia (Kerekes *et al*., 1986), however, estimates that for an increase of one Hazen unit, the increase in DOC concentration is more than twice the increase in DOC estimated here. The difference in intercept and slope between these reports (Equations 6.4.1 and 6.4.2) and the relationship found here (DOC concentration = 3.89 + 0.044 * Hazen) may arise as the water sampled here was sourced from high-order drainage channels from predominantly peat-covered catchments. These waters may be less affected by water draining from less peat-dominated areas that may contribute other, non-humic DOC.

$$\text{DOC concentration} = 1.09 + 0.051 * \text{Hazen} \quad (6.4.1)$$

$$\text{DOC concentration} = 2.7 + 0.115 * \text{Hazen} \quad (6.4.2)$$

Seasonal variation in the water colour-DOC relationship was not found to be significant for water samples collected in the four months examined here, however, seasonal variation has been identified in the colour-DOC relationship for interstitial peat waters, and has been attributed to contribution of 'colourless', non-humic DOC (e.g. Wallage *et al*., 2006). The concentration of humic substances in water determined from measurement as Hazen may therefore provide more accurate representation of DOC derived from peat decomposition relative to direct DOC assay. As the estimation of DOC concentration used in analysis here is essentially a linear transform of Hazen values, the relationships identified are, of course, the same as those that would be identified had land use/management variables been regressed against Hazen. Any relationships identified in this study could therefore be considered to be between land use on blanket peat and the relative differences in water colour between catchments. As organic colour in water is derived primarily from humic substances (Aiken *et al*., 1985), the colour-DOC relationship indicates that the dominant component of DOC identified for the catchments sampled in Chapter 5 are humic substances.

The identification of a relationship between the cover of blanket peat and drainage DOC concentration for the nine catchments examined here provides further evidence of the link between the amount of carbon available for release as DOC (or CO_2) should it begin to decompose and DOC concentrations in drainage. However, the cover of blanket peat was not automatically selected by multiple regression and the peat-DOC relationship was only found to be significant in two of the five analyses undertaken (r^2=0.37-0.48). It may be worthy of note that one of the catchments studied here, Midhope, although containing 36% cover of blanket peat, fell consistently below the modelled slope in all regression analyses of new burn on blanket peat against mean DOC concentration (Figures 6.3.2-6.3.5). This could possibly indicate uncertainty about the amount of blanket peat cover within Midhope catchment. In fact there are records of several severe wildfires occurring within Midhope catchment since 1887. Radley (1965) notes that 15 years after a wildfire in 1939, the area on Pike Lowe was still “bare”. Pike Lowe is an area in Midhope catchment identified by digital soil data as containing blanket peat; however, from contemporary aerial photography large outcrops of rock and mineral soil are visible.

It should also be noted that the number of catchments examined (nine) was limited due to the need to ensure that the area of catchment contributing to measured samples was accurate. Despite the limited number of catchments examined, a statistically significant relationship between the proportion of new burn on blanket peat and drainage DOC concentration was identified in all analyses undertaken. For each year examined, the regression models for new burn on blanket peat against annual mean DOC and mean DOC derived for a limited number of months explained a consistent degree of variation in DOC concentration (r^2=0.59-0.63, 1999; r^2=0.60-0.64, 2005). This indicates that missing periods of data did not in this case significantly influence the relative differences in DOC concentration determined between catchments. This could also indicate that the effect of burning on drainage DOC concentration has not changed between the two years examined, while the influence of the percent cover of blanket peat on DOC appears to have reduced from r^2=0.48 in 1999 to r^2=0.37 in 2005.

Owing to gaps in the colour record for Keighley Moor and Watersheddles reservoirs, comparison of changes in the relationship between new burn on blanket peat and annual mean drainage DOC concentration between years for all nine reservoirs cannot be quantified. However, Figure 6.3.5 provides a qualitative assessment of the relative burn-DOC relationship for each catchment for 1999 (six month mean DOC) and 2005 (eight month mean DOC). For Lower Laithe, Cod Beck/Oakdale and Watersheddles catchments, where small (0.1 ha) or no change in the area of new burn on blanket peat was determined, DOC concentrations changed by between 0.02-0.2 mg l^{-1} (Table 6.2.3). For the remaining six catchments, where changes in the area of new burn were determined to be at least 1% of the catchment, the changes in DOC were significantly higher ranging from between 0.39-2.18 mg l^{-1}. Although mean DOC concentrations for each year were determined for different averaging periods (six or eight months), the data suggest that greater changes in DOC concentration occur for catchments where burn management is increasing. The data for Ponden catchment are not consistent with observations for the other catchments as DOC concentrations appear to have decreased by 0.6 mg l^{-1}. There may however be ambiguity as to whether water is pumped directly from parts of Ponden catchment to Watersheddles WTW (Banks, 2009). These catchments were included in the analysis to retain a higher number of observations. Of particular note is the comparison of data for Watersheddles and Keighley Moor catchments located less than 5 km apart in West Yorkshire. Of the eight catchments examined, these two catchments contain the highest percent cover of blanket peat: 83% and 96% respectively. DOC concentrations appear significantly lower for Keighley Moor in 1999 compared to Watersheddles, and burn management on blanket peat accounts for 4% of Keighley Moor compared to 7% for Watersheddles. In 2005 burn management in Keighley Moor increases to a level comparable to that in Watersheddles (7% and 8% respectively) as do DOC concentrations.

That the proportion of new burn on blanket peat was the only factor entered into multiple regression in each analysis indicates that the effect of burning on DOC production and release from underlying soils as identified for small headwater catchments (<3 km^2) translates into a measurable landscape-scale (1.5-21 km^2) phenomenon. This shows that burn management on blanket peats can influence one of the key ecosystem services provided by upland areas, that of potable water supply. It can also therefore be implied that the costs associated with water treatment arise partly from catchment land use decisions.

6.5. Conclusion

The data presented in this chapter show that the proportion of new burn on blanket peat is the most significant predictor of spatial variance in drainage DOC concentration for the nine upland reservoir catchments examined in the South Pennines for 1999 and 2005. This indicates that the effect of burning on DOC production and release from underlying soils as identified for small headwater catchments (<3 km^2) translates into a measurable landscape-scale (1.5-21 km^2) phenomenon of direct relevance to water utility companies. Most importantly, where no increase in burn area was seen between 1999 and 2005, increases in DOC were minimal. There is therefore a need to understand whether changes in the extent of burn management over time relate to changes in DOC concentration reported for upland peat catchments over the recent past. This will now be examined in Chapter 7.

Chapter 7: Temporal variation in DOC production and release from upland peat soils.

7.1. Introduction

Increasing trends in DOC concentration have been observed in surface waters in Canada (Bouchard, 1997), northern and eastern USA (Stoddard *et al*., 2003), the Czech Republic (Hejzlar *et al*., 2003), Norway (Hongve *et al*., 2004), Finland (Vuorenmaa *et al*., 2006) and the UK (Freeman *et al*., 2001a; Worrall *et al*., 2004). Those observed in the UK, however, have been notably larger (Skeljkvale *et al*., 2005), with mean concentrations in rivers and lakes draining upland catchments increasing by 91% from 1988-2003 (Evans *et al*., 2005). Longer term data (e.g. Watts *et al*., 2001; Worrall *et al*., 2003b) suggest that these are part of a trend detectable since at least the 1970s and represent real increases in carbon loss rather than changes in discharge (e.g. Tranvik and Jansson, 2002), as both DOC concentration and flux have risen (e.g. Worrall *et al*., 2003b).

There has been considerable debate over the last decade regarding factors that might underlie the observed increases in DOC from peat soils. These include climatic change (Freeman *et al*., 2001a; Stoddard *et al*., 2003; Worrall *et al*., 2003b; Evans *et al*., 2005) and associated increases in enchytraied worm activity (Cole *et al*., 2002; Carrera *et al*., 2009), increasing atmospheric CO_2 (Freeman *et al*., 2004), hydrological change (Hongve *et al*., 2004; Evans *et al*., 2005), artificial drainage (Worrall *et al*., 2003b), severe drought events (Watts *et al*., 2001; Worrall and Burt, 2004), the removal of decomposition inhibiting phenolic compounds following prolonged water table drawdown (Freeman *et al*., 2001b), decreasing acid deposition (Stoddard *et al*., 2003;

Evans *et al*., 2006; Vuorenmaa *et al*. 2006; Monteith *et al*., 2007) and increasing N deposition (Findlay, 2005; Bragazza *et al*., 2006).

The widespread occurrence of increasing trends in DOC suggest that global and regional scale phenomena are important (Evans *et al*., 2008), yet they do not explain the markedly greater increase (Skjelkvåle *et al*., 2005) or the significant variation between adjacent blanket peat catchments (Chapter 5) observed in the UK. For example, changes in sulphate and chloride deposition combined with a catchment acid sensitivity index could explain trends in DOC in north-eastern USA, Ontario/Quebec, Atlantic Canada, southern Nordic and northern Nordic regions, but not in the UK (Monteith *et al*., 2007). Additionally, out of 315 sites examined across the UK (Worrall *et al*., 2007), 18% have shown significant decreases in DOC concentration over the last ten years, including a number of peat-dominated catchments. These observations suggest that more localised factors may be contributing to the UK increases (Worrall *et al*., 2003b; Evans *et al*., 2005). The area of new vegetation burn on blanket peat within catchments was identified as the most significant predictor of spatial variance in contemporary (2005) DOC concentration from both small headwater (<3 km^2; Chapter 5) and reservoir (1.5-20 km^2; Chapter 6) catchments. The use of controlled burning as a management tool has almost doubled in some areas of the English uplands since the 1970s (Yallop *et al*., 2006a), and could indicate a possible causative link with the long term increases in DOC.

To fully understand the potential role of changes in regional and localised factors on DOC concentrations, large-scale controlled experimentation would provide an ideal approach. Unfortunately no projects of this type have been undertaken, and neither are there abundant long-term data for DOC loss from upland catchments. However, water utility colour data, which provide a proxy for DOC concentration records (Kerekes *et al*., 1986; Eatherall *et al*., 1998; Worrall *et al*., 2003), provide a good historical record and in places date back to the 1960s. The main sources of DOC to upland drainage waters are organic soils (Urban *et al*., 1989), and are derived primarily as a consequence of the decomposition of blanket peats (McDonald *et al*., 1991). Peat decomposition produces a range of organic fractions including humic substances, which impart organic 'colour' to waters (Aiken *et al*., 1985). The highly significant relationship between water colour (Hazen) and DOC concentration found in 181 samples from 50 catchments sampled in 2005 (Chapter 6.3.1) indicates that humic substances comprise the main component of drainage DOC from upland peat catchments examined in this study. Measurements of water colour would therefore appear appropriate to provide data on drainage DOC trends in this type of environment.

Partial aerial photographic mapping surveys have been conducted in the UK since the 1940s, with further surveys commissioned over upland areas within National Parks (e.g. Taylor *et al*., 2000). This archive of aerial imagery available provides a good record of changes in land cover over the past few decades. In addition to long-term records of climatic data available for the UK (e.g. the British Atmospheric Data Centre (BADC), http://badc.nerc.ac.uk), atmospheric deposition data have been monitored since 1986 by the UK Air Quality Archive (http://www.airquality.co.uk).

The aim of the work presented in this chapter is to use these data sources to reconstruct DOC concentrations for a series of upland peat catchments in the southern Pennines and identify any relationships between extrinsic factors (climate and acid deposition), intrinsic factors (land use/management) and DOC concentrations over the last 40 years. Factors controlling the increasing trends in the UK are still not fully understood, and this chapter will provide valuable contribution to this area of current debate.

The objectives defined for this chapter were:

i. identify a series of catchments where both long term colour data and historical aerial imagery were available;
ii. derive DOC time series for catchments identified;
iii. obtain data on extrinsic factors for all catchments to include rainfall, temperature and sulphate deposition;
iv. examine changes in extrinsic factors and their relationship to changes in DOC;
v. identify land use changes over the last 40 years and identify any relationships with drainage DOC.

7.2. Methods

7.2.1. Study catchments

Historical water colour data spanning at least 10 years and good coverage of historical aerial photography were identified for five of the topographically defined reservoir catchments examined in Chapter 6 (Table 7.2.1). These five catchments are grouped in two discrete areas of the South Pennines in Yorkshire (Figure 7.2.1). The southern group contains three adjacent catchments that supply Agden, Broomhead and Langsett reservoirs. The two catchments comprising the northern group are located less than 5 km apart and supply Lower Laithe and Keighley Moor reservoirs (Figure 7.2.1). By area the catchments contain significant amounts of blanket peat (between 22-96%) and are all underlain by the Millstone Grit series (BGS DiGMapGB data 1:625,000).

Table 7.2.1. Availability of historical aerial photography, water colour, climatic and atmospheric deposition data for study catchments.

Reservoir catchment	Water colour (DOC)	Rainfall and temperature	Acid deposition	Aerial photographic capture
Agden	1961 - 2006	1961 - 2006	1986 - 2006	1966, 1976, 1989, 1995, 1999, 2001, 2005
Broomhead	1961 - 2006	1961 - 2006	1986 - 2006	1968, 1976, 1989, 1995, 1999, 2001, 2003, 2005
Langsett	1961 - 2006	1961 - 2006	1986 - 2006	1968, 1976, 1989, 1995, 1999, 2001, 2005
Keighley Moor	1990 - 2006	1973 - 2006	1986 - 2006	1990, 1999, 2002, 2005
Lower Laithe	1994 - 2006	1973 - 2006	1986 - 2006	1993, 1999, 2002, 2005

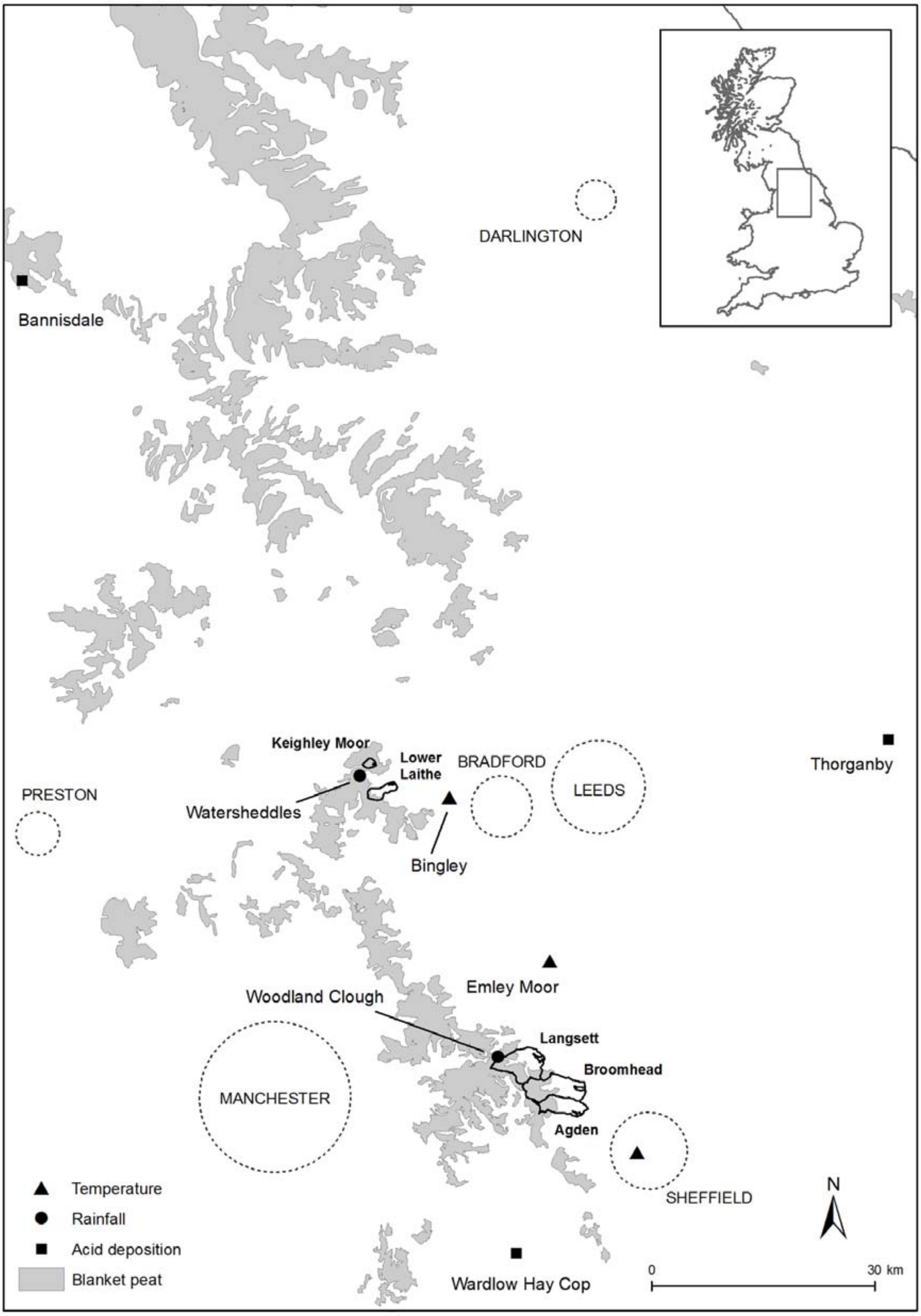


Figure 7.2.1. Location of study catchments and nearest rainfall, temperature and acid deposition monitoring stations.

7.2.2. Reconstruction of DOC record

For the northern group of catchments, water colour measurements were available as Hazen units from January 1990 to September 2005 (Keighley Moor) and December 1993 to December 2005 (Lower Laithe). There were often breaks in the colour record for Keighley Moor (1999 onwards) when no measurements were recorded. Where data were available, mean monthly colour was calculated for all months in each data record. DOC concentration was then estimated using the relationship between DOC concentration and Hazen (Figure 7.2.2; Equation 7.2.1) determined in Chapter 6.3.1 across samples for all catchments examined in Chapter 5.

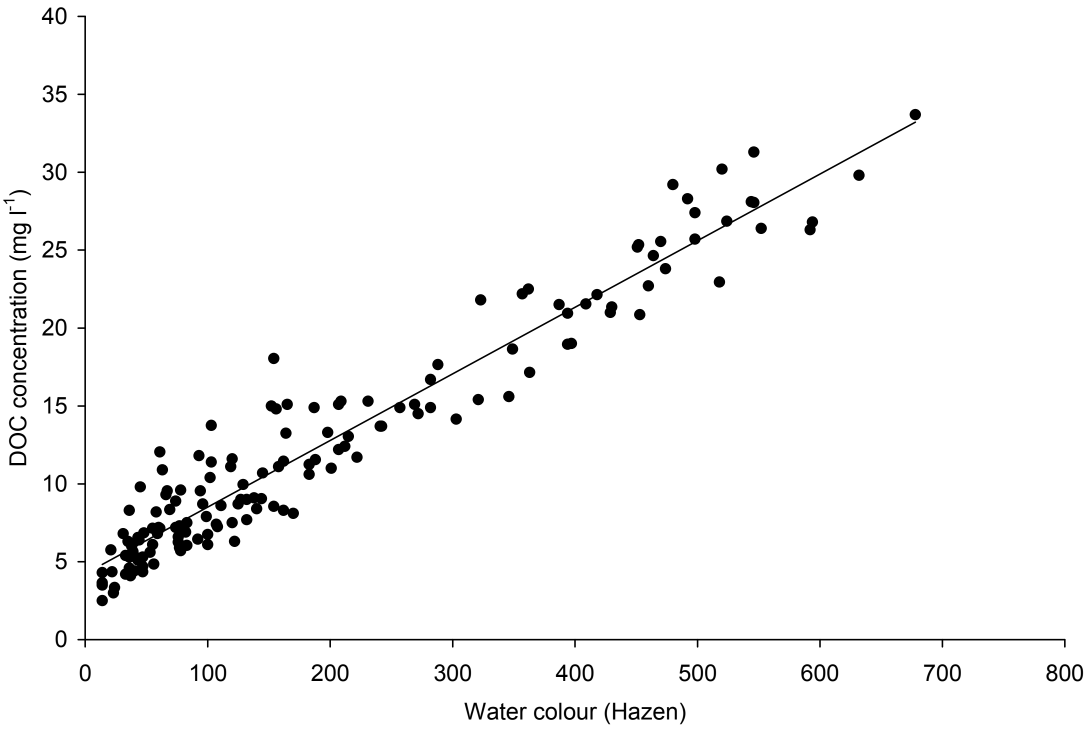


Figure 7.2.2. Water colour determined in Hazen against DOC concentration in drainage for 50 catchments sampled in 2005 (r^2=0.93, p<0.001; Chapter 6.3.1).

$$\text{DOC concentration} = 0.044 * \text{Hazen} + 3.89 \quad (7.2.1)$$

For the three catchments in the southern group (Agden, Broomhead and Langsett), monthly water colour measurements were available from September 1974 to December 2005. In addition, mean annual (calendar year) colour values for the years 1961 to 1979 were available from published data in McDonald *et al*. (1991). Although colour was largely recorded as Hazen units during this time, for the period March 1979 to December 1989 colour was determined as absorbance units measured at 400 nm. Owing to this mixture of record type, DOC concentrations for these catchments were determined in two stages. Firstly colour data measured in absorbance were converted to Hazen following the method outlined by Watts *et al*. (2001) to produce a consistent monthly time-series of colour in Hazen (1974-2005; see Chapter 3.5.1). DOC concentration was then estimated using Equation 7.1.

7.2.3. Climatic data

Meteorological data were sourced from the British Atmospheric Data Centre (http://badc.nerc.ac.uk).

7.2.3.1. Rainfall data

Long-term rainfall measurements were obtained from the meteorological station with a complete record nearest to each catchment group (Figure 7.2.1). For the northern group, this is located at Watersheddles reservoir (1973-2006) within 3 km of each catchment at 340 m above sea level. The nearest monitoring station to the southern group is located at Woodland Clough (1962-2006) on the watershed of Langsett catchment at 438 m above sea level. Monthly and annual rainfall totals were calculated for each year.

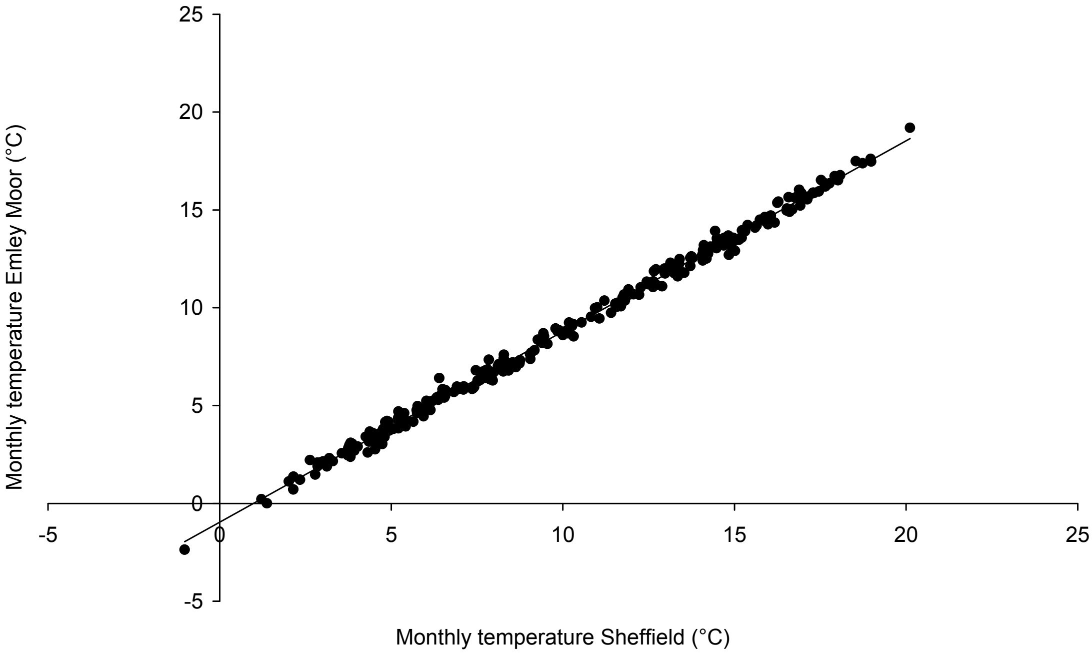
7.2.3.2. Temperature data

The nearest meteorological stations with complete records of air temperature were identified for each catchment group (Figure 7.2.1). The nearest monitoring station to the northern group is located 10 km to the east in open fields near Bingley (262 m above sea level). Temperature data measured at this monitoring station were obtained from 1973-2005. For the southern group, the nearest monitoring station is located in Sheffield at a distance of 15 km (1961-2005). Temperatures recorded in urban areas are potentially higher than those affecting upland areas owing to urban heat island effects (e.g. Oke, 1982) and, in this case, adiabatic change. Two approaches were therefore adopted to calibrate the urban derived data. Firstly, shorter-term data (1984-2005) were obtained from the monitoring station on Emley Moor situated in a moorland environment 15 km to the north of the study catchments (259 m above sea level). These data were used to model the difference in temperature measured at Sheffield over the same period due to the effects of urban heat islands (Figures 7.2.3a and 7.2.3b). The derived relationship between mean monthly temperatures measured at Emley Moor and those measured at Sheffield (Equation 7.2.2) were then used to adjust the temperature record at Sheffield for the missing period (1961-1984) at Emley Moor. To account for adiabatic change, analyses were undertaken using the temperature anomaly from the long-term (1975-2005) mean rather than absolute values.

$$T_{Em} = (T_{Sheff} * 0.975) - 0.964 \qquad (7.2.2)$$

where T_{Em} is mean monthly temperature at Emley Moor and T_{Sheff} is mean monthly temperature at Sheffield.

a)



b)

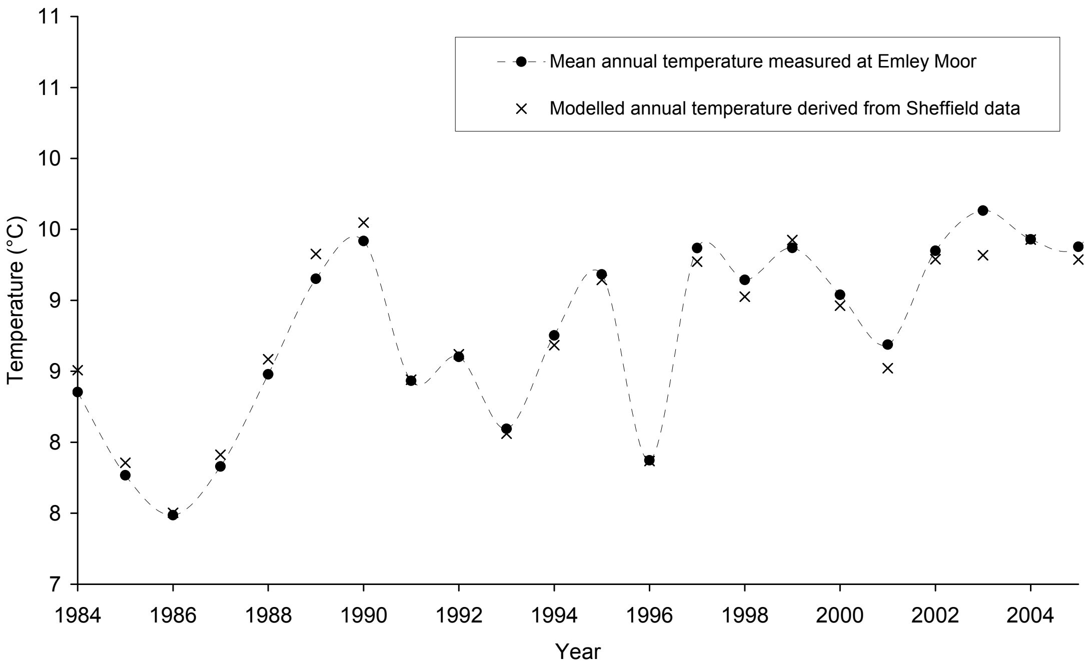


Figure 7.2.3. a) Mean monthly temperatures recorded at Emley Moor against mean monthly temperatures recorded at Sheffield for the period 1984-2005 (r^2=0.996, p<0.001, n=276);
b) Mean annual temperature recorded at Emley Moor and modelled annual temperature derived from Sheffield data.

7.2.3.3. Confidence in temperature record

Daily mean temperatures for each monitoring station were calculated as the average of daily minima and maxima following the method in Holden and Adamson (2002). Monthly and annual mean temperatures were derived from these daily means. No indication of instrumentation change or replacement was given from the BADC to allow consistency of the measurements to be made. However, mean annual temperatures derived at Bingley and Emley Moor for the period 1973 to 2005 are significantly correlated (correlation coefficient = 0.984, $p<0.001$; Figure 7.2.4). The concordance between the inter-annual variability in temperatures determined for both meteorological stations suggests no artefacts or anomalies in temperature data used for analysis here can be attributed to the method of temperature measurement.

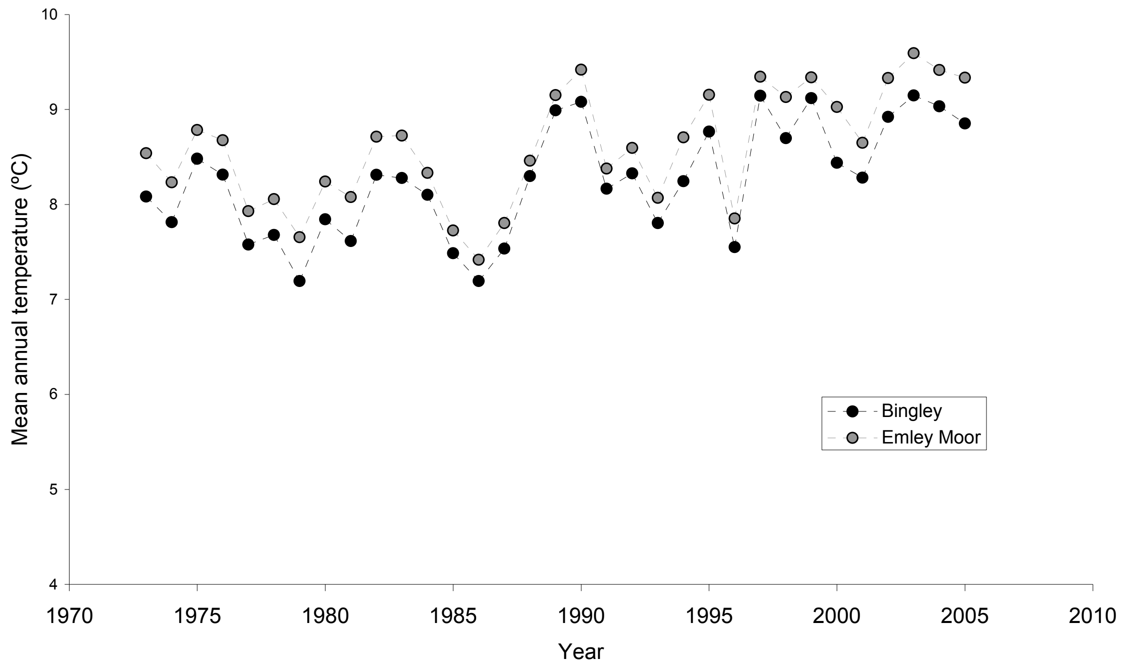


Figure 7.2.4. Mean annual temperatures for Bingley and Emley Moor for 1973-2005.

7.2.4. Acid deposition data

Wet deposition sulphate data were sourced from the UK Air Quality Archive (http://www.airquality.co.uk) for the nearest monitoring stations in the Acid Deposition Monitoring Network (ADMN). As the nearest monitoring station to the northern catchment group is located more than 60 km to the south, monthly deposition amounts (mg m^{-2}) for this group were estimated by applying an inverse distance weighted algorithm (Shepard, 1968; Chapter 3.6.3) to data from the three nearest stations: Wardlow Hay Cop, Thorganby and Bannisdale (Figure 7.2.1; Table 7.2.2). Monthly deposition data for the southern catchment group were obtained from the Wardlow Hay Cop monitoring station located less than 20 km to the south of this catchment group.

Table 7.2.2. Inverse distance weighting applied to wet deposition sulphate data for northern group of catchments.

Acid deposition monitoring station	Distance (km)	IDW weight
Wardlow Hay Cop	66.4	0.39
Thorganby	68.8	0.36
Bannisdale	81.8	0.25

7.2.5. Land cover and soil distribution data

Aerial imagery covering each catchment for all available years (Table 7.2.1) were scanned and orthocorrected (see Chapter 3.2.1). Land cover classes defined for reservoir catchments in the Chapter 6.2.4, namely unimproved grassland, semi-improved grassland, coniferous plantation, broadleaf woodland, ericaceous dominated (predominantly *Calluna*) and grass/sedge dominated moorland were mapped in each year of imagery using ArcGIS. Areas of vegetation burn Class 1 and burn Class 2 (Chapter 3.2.2) were mapped within areas of ericaceous and grass/sedge moorland for each year.

Soils present within each catchment were identified by intersecting NSRI digital soil data derived from Mackney *et al*. (1983) with the catchment boundaries. These were subsequently categorised into three broad soil types: blanket peat (1011b); upland soils with peaty topsoils (651a and 721b) and non-peaty soils (541f, 541g, 712a and 713g), following the descriptions given by Avery (1980). The areal extent of all combinations of land use, management and soil type present in each catchment were then derived by year of imagery (Table 7.2.3).

Table 7.2.3. Land use and management variables in each catchment by soil type (area in km^2 shown). CL1: Class 1 burn; CL2: Class 2 burn; CM: *Calluna* moorland; GM.: Grass/sedge moorland; BW: Broadleaf woodland; IG: Improved grass; PL: Plantation; UG: Unimproved grass.

Soil type		**Blanket Peat**				**Upland peat soils**							**Non peaty soils**			
Land use		**CL1**	**CL2**	**CM**	**GM**	**BW**	**CL1**	**CL2**	**CM**	**IG**	**PL**	**GM**	**BW**	**IG**	**PL**	**UG**
Agden	**1966**	0.12	0.36	3.58	0.60	0.56	0.28	0.46	2.58	1.16	0.36	2.13	0.02	0.58	0.19	0.21
Catchment area – 12.23	**1976**	0.20	0.41	3.60	0.58	0.57	0.21	0.36	2.58	1.16	0.36	2.13	0.02	0.58	0.19	0.21
Reservoir – 0.24	**1989**	0.41	0.26	3.76	0.42	0.57	0.44	0.10	2.52	1.16	0.39	2.14	0.02	0.58	0.20	0.20
	1995	0.62	0.17	3.77	0.41	0.57	0.46	0.18	2.51	1.16	0.39	2.16	0.02	0.58	0.20	0.20
	1999	0.74	0.29	3.78	0.40	0.63	0.65	0.15	2.32	1.13	0.40	2.31	0.03	0.56	0.21	0.21
	2001	0.71	0.14	3.77	0.41	0.63	0.64	0.12	2.33	1.13	0.40	2.31	0.03	0.56	0.21	0.21
	2005	0.88	1.42	3.92	0.26	0.68	0.38	0.91	2.22	1.13	0.39	2.36	0.03	0.56	0.21	0.21
Broomhead	**1968**	0.01	0.56	7.45	1.59	0.58	0.03	0.16	2.61	1.67	1.27	2.65	0.40	1.80	0.15	0.37
Catchment area – 21.41	**1976**	0.20	0.21	7.49	1.55	0.64	0.03	0.16	2.70	1.72	1.21	2.50	0.38	1.79	0.13	0.43
Reservoir – 0.50	**1989**	0.31	0.28	7.68	1.36	0.73	0.23	0.27	2.63	1.63	1.54	2.24	0.43	1.79	0.16	0.36
	1995	0.81	1.08	7.87	1.17	0.76	0.38	0.35	2.63	1.58	1.55	2.25	0.45	1.72	0.18	0.37
	1999	1.22	1.40	7.94	1.10	0.77	0.58	0.33	2.64	1.57	1.59	2.21	0.45	1.76	0.18	0.34
	2001	1.25	1.24	7.95	1.09	0.94	0.58	0.24	2.59	1.53	1.59	2.12	0.48	1.73	0.18	0.33
	2003	1.26	1.63	7.98	1.05	0.90	0.55	0.56	2.70	1.53	1.59	2.05	0.47	1.73	0.18	0.35
	2005	2.86	1.79	8.02	1.02	0.84	0.90	0.82	2.76	1.56	1.59	2.03	0.47	1.73	0.19	0.33
Langsett	**1968**	0.13	0.16	6.63	4.08	0.00	0.09	0.27	2.92	0.76	0.30	4.33	0.00	0.87	0.39	0.08
Catchment area – 20.98	**1976**	0.45	0.53	7.06	3.65	0.00	0.19	0.64	2.91	0.70	0.58	4.12	0.00	0.80	0.50	0.04
Reservoir – 0.53	**1989**	0.83	0.69	7.14	3.56	0.00	0.47	0.31	3.09	0.58	0.74	3.91	0.00	0.64	0.65	0.05
	1995	1.06	0.63	7.67	3.00	0.00	0.87	0.32	3.39	0.60	0.75	3.57	0.00	0.64	0.61	0.09
	1999	1.34	1.34	7.78	2.91	0.00	1.00	0.63	3.22	0.60	0.77	3.74	0.00	0.64	0.64	0.06
	2001	1.14	1.10	8.27	2.41	0.00	0.75	0.46	3.39	0.59	0.77	3.56	0.00	0.64	0.64	0.06
	2005	1.45	1.38	8.36	2.33	0.00	0.95	0.84	3.61	0.61	0.79	3.31	0.00	0.64	0.67	0.03
Keighley Moor	**1990**	0.02	0.12	1.02	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Catchment area – 1.54	**1999**	0.06	0.04	1.04	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Reservoir – 0.07	**2002**	0.07	0.03	1.04	0.44	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	2005	0.12	0.07	1.05	0.42	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Lower Laithe	**1994**	0.00	0.00	0.43	0.69	0.02	0.09	0.07	1.66	0.13	0.01	1.06	0.03	0.71	0.05	0.06
Catchment area – 5.00	**1999**	0.00	0.00	0.42	0.69	0.02	0.19	0.13	1.68	0.13	0.01	1.04	0.03	0.71	0.05	0.06
Reservoir – 0.13	**2002**	0.00	0.00	0.42	0.69	0.02	0.15	0.11	1.59	0.13	0.01	1.13	0.03	0.71	0.05	0.06
	2005	0.00	0.00	0.42	0.69	0.02	0.06	0.20	1.61	0.13	0.01	1.11	0.03	0.71	0.05	0.06

7.2.6. Data summary and statistical analysis

The datasets collated for analysis were available as either continuous time series (DOC concentration, temperature, rainfall and sulphate deposition) or discrete data (land use). Each data type was treated accordingly. As the peak in colour/DOC coincides with the division between water years, annual mean values determined in this analysis were based on the calendar year. All statistical analyses were performed using SPSS v16.0.

Detection of trends in continuous time series data

Trends in monthly DOC concentration, temperature, rainfall and wet deposited sulphate were assessed using the seasonal Kendall test (Hirsch *et al*., 1982; Chapter 3.6.2). This test was performed on data from all catchments for the period January 1990 to December 2005. For Agden, Broomhead and Langsett catchments it was possible to extend this trend analysis to the period January 1975 to December 2005 for DOC concentration, temperature and rainfall and this was undertaken. As DOC concentration data from 1961-1974 were only available as annual mean values, trend analysis was not performed on data for this earlier period.

Identification of relationships between extrinsic/intrinsic factors and DOC concentration

Owing to the limited availability of wet deposited sulphate data (1986 onwards) and land use/management observations, the following approaches to analysis were undertaken:

1. Annual temperature anomalies from the long-term (1975-2005) mean, annual rainfall and annual deposited sulphate were independently regressed against annual mean DOC concentration in each catchment for all years of DOC data available from 1986-2005. Owing to breaks in data recorded for Keighley Moor, a three month mean DOC concentration was calculated on colour data for the months February, April and June (FAJ), as these monthly measurements were consistently available in each year.
2. For Agden, Broomhead and Langsett catchments, annual temperature anomalies and annual rainfall were regressed against annual mean DOC concentration for all years from 1961-2005.
3. Antecedent temperatures (e.g. Adamson *et al*., 2001; Clarke *et al*., 2005) and rainfall (e.g. Mitchell and McDonald, 1992) have been identified as potential drivers of DOC concentration. Therefore annual mean temperature anomalies and annual rainfall lagged by periods of 1-3 years were regressed against DOC concentration in steps 1 and 2 above.
4. The potential effects of climatic and acid depositional factors were examined by entering temperature anomalies and rainfall (including lagged periods) and sulphate deposition data for all catchments from 1986-2005 into forward-entry multiple regression.
5. To provide the largest number of land/use management observations for a consistent period across all catchments, all data for the years 1989-2005 were combined. All land use/management variables (Table 7.2.3) were regressed against mean DOC concentration using forward-entry stepwise regression. As this analysis included five catchments of different size and areas of deep peat, areas of each factor were

converted to proportions and normalised prior to analysis using the arcsine-square root transformation (Fowler and Cohen, 1990; Chapter 3.6.1). Mean DOC was first calculated for the three months (FAJ) consistently available in each year for the record at Keighley Moor.

6. Analysis in step 5 was repeated using annual (12 month) mean DOC concentrations for all catchments. This excluded two of the years of land use observation for Keighley Moor.
7. The land use factor identified as significant for all catchments was then tested in each catchment using linear regression against annual DOC concentration.

7.3. Results

7.3.1. Changes in DOC concentration

For all five catchments examined, highly significant (p<0.001) increasing trends in DOC concentration were identified for the period January 1990 to December 2005 (Figures 7.3.1-7.3.5). Trend magnitude ranged from 0.09 to 0.33 mg l^{-1} yr^{-1} (median values), representing increases of 18-94% relative to 1990-1994 means (Table 7.3.1). In the longer-term data (January 1975 to December 2005), highly significant (p<0.001) increasing trends in DOC were identified in the three catchments examined. The magnitude of the trends identified within these three catchments for the period 1990-2005 (0.20-0.33 mg l^{-1} yr^{-1}) were more than double those identified over the longer-term (0.08-0.14 mg l^{-1} yr^{-1}).

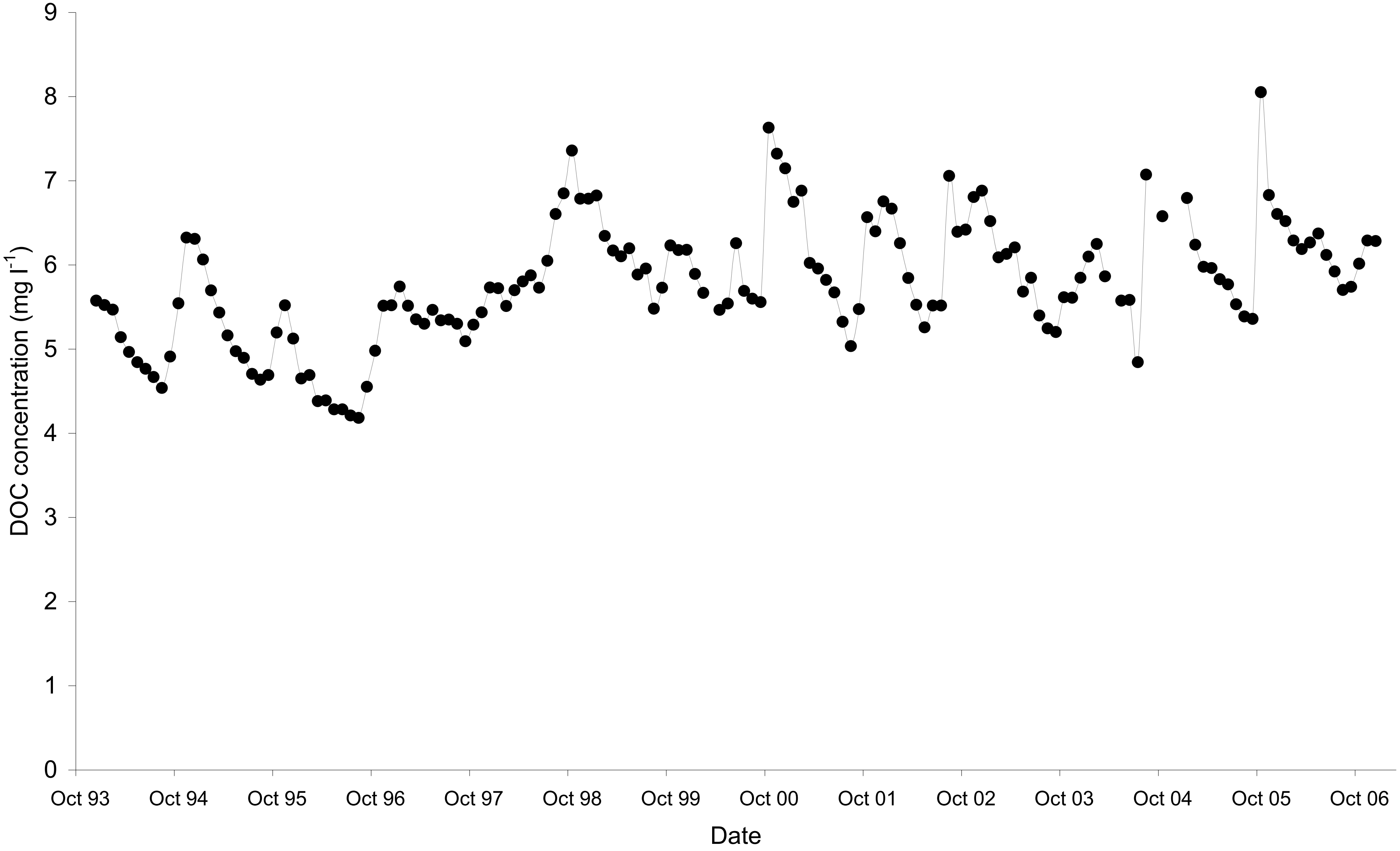


Figure 7.3.1. Monthly mean DOC concentration in water sampled at Lower Laithe WTW.

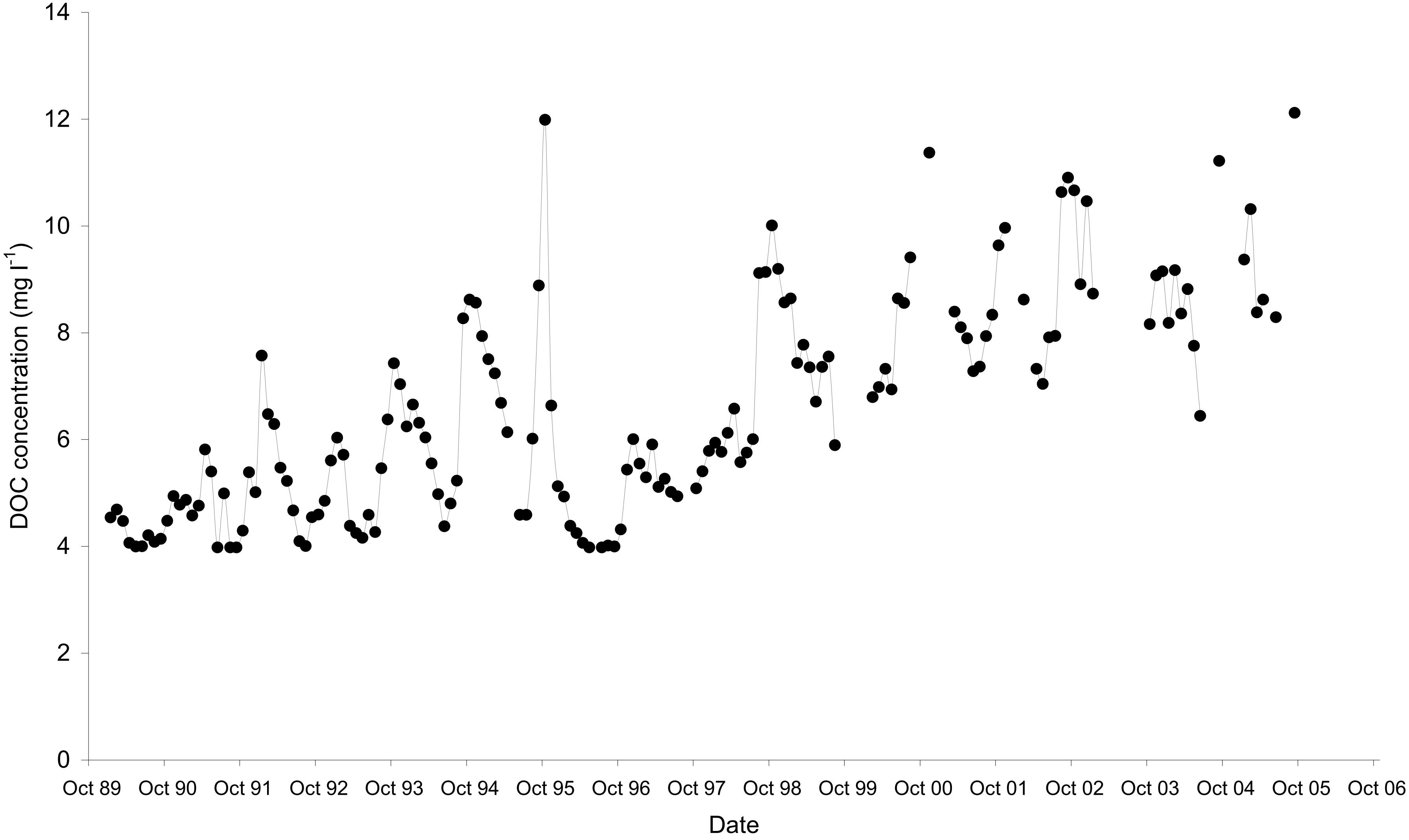


Figure 7.3.2. Monthly mean DOC concentration in water sampled at Keighley Moor WTW.

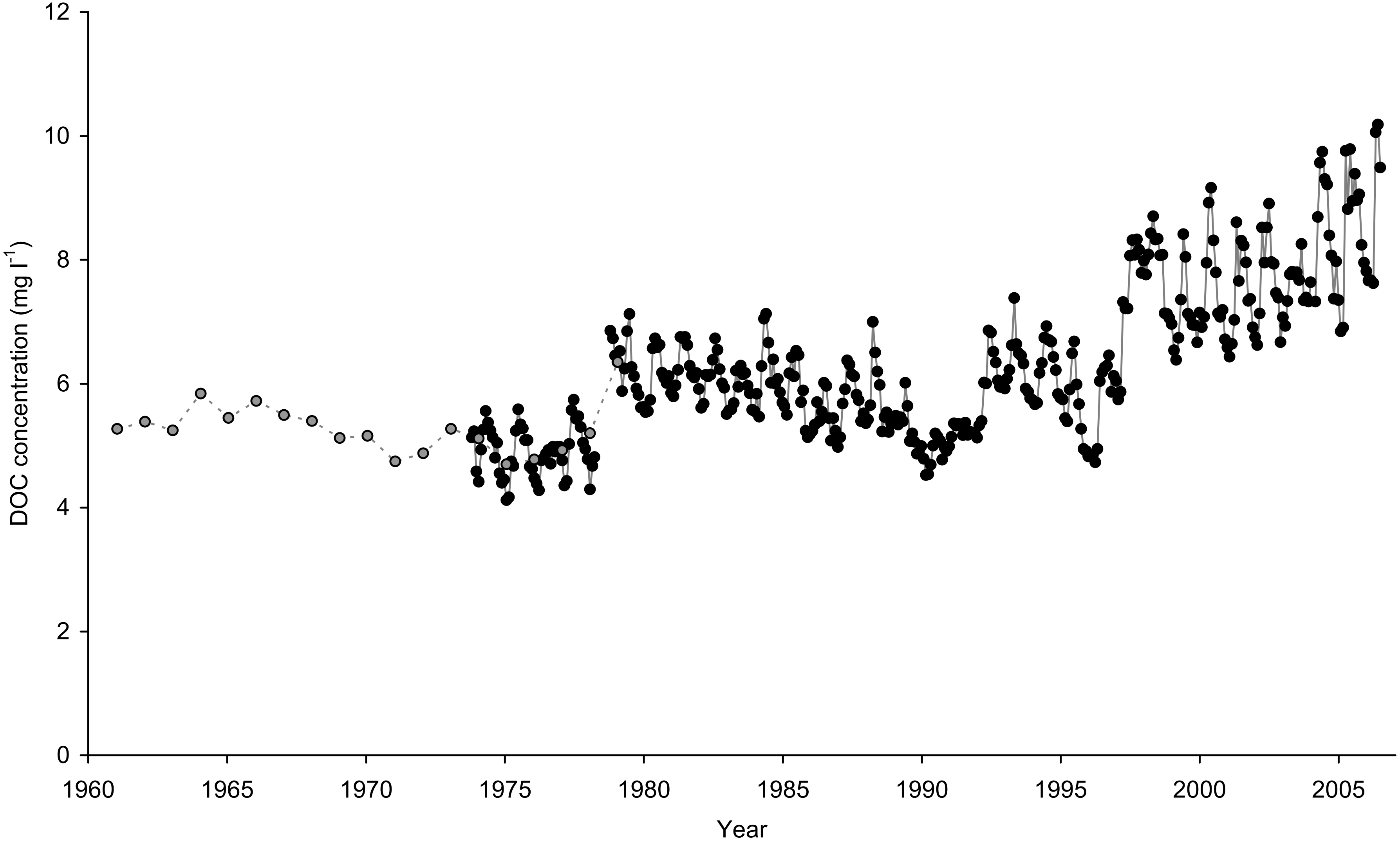


Figure 7.3.3. Monthly mean DOC concentration in water sampled at Agden WTW (solid circle; grey circle shows annual mean data).

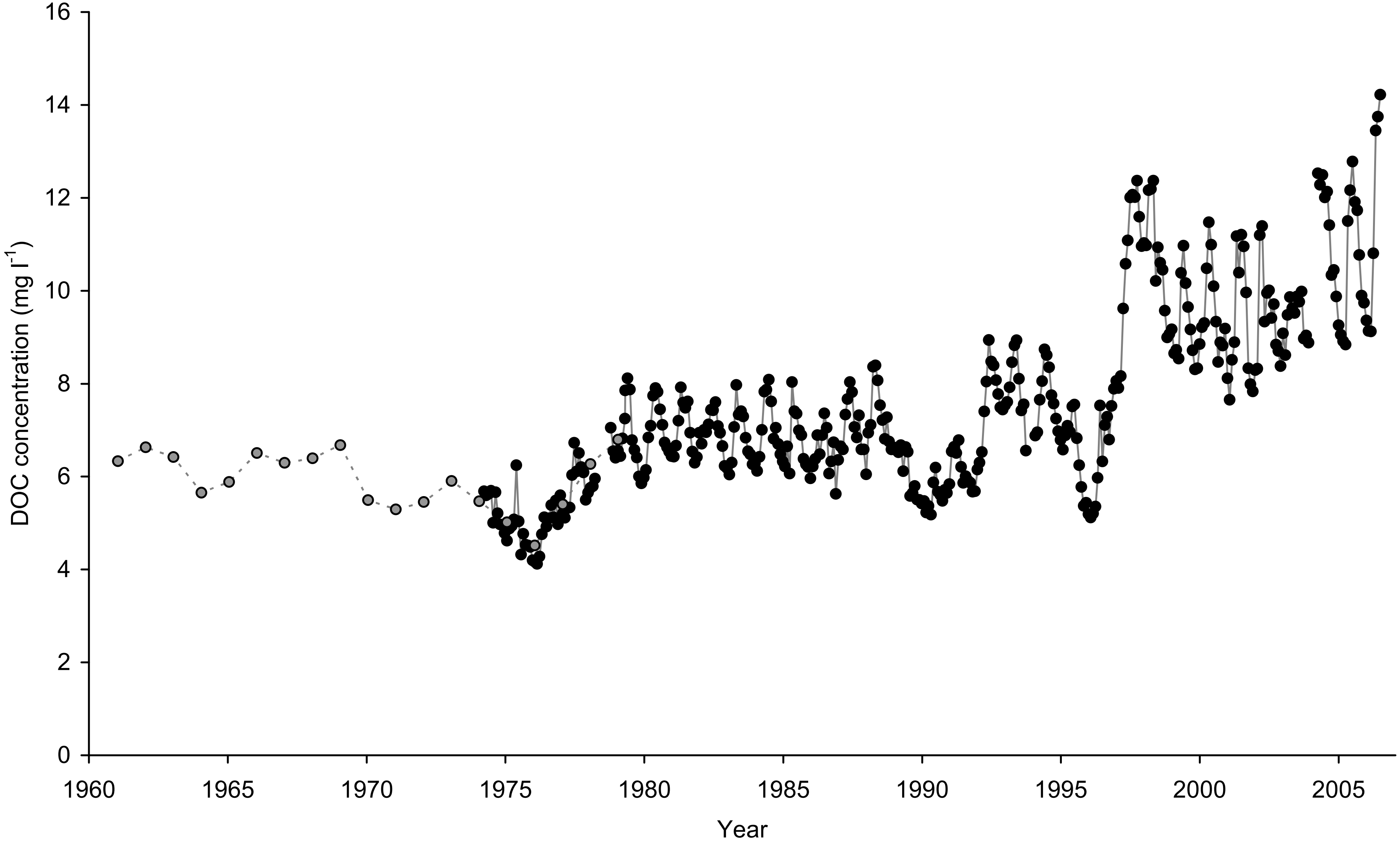


Figure 7.3.4. Monthly mean DOC concentration in water sampled at Broomhead WTW (solid circle; grey circle shows annual mean data).

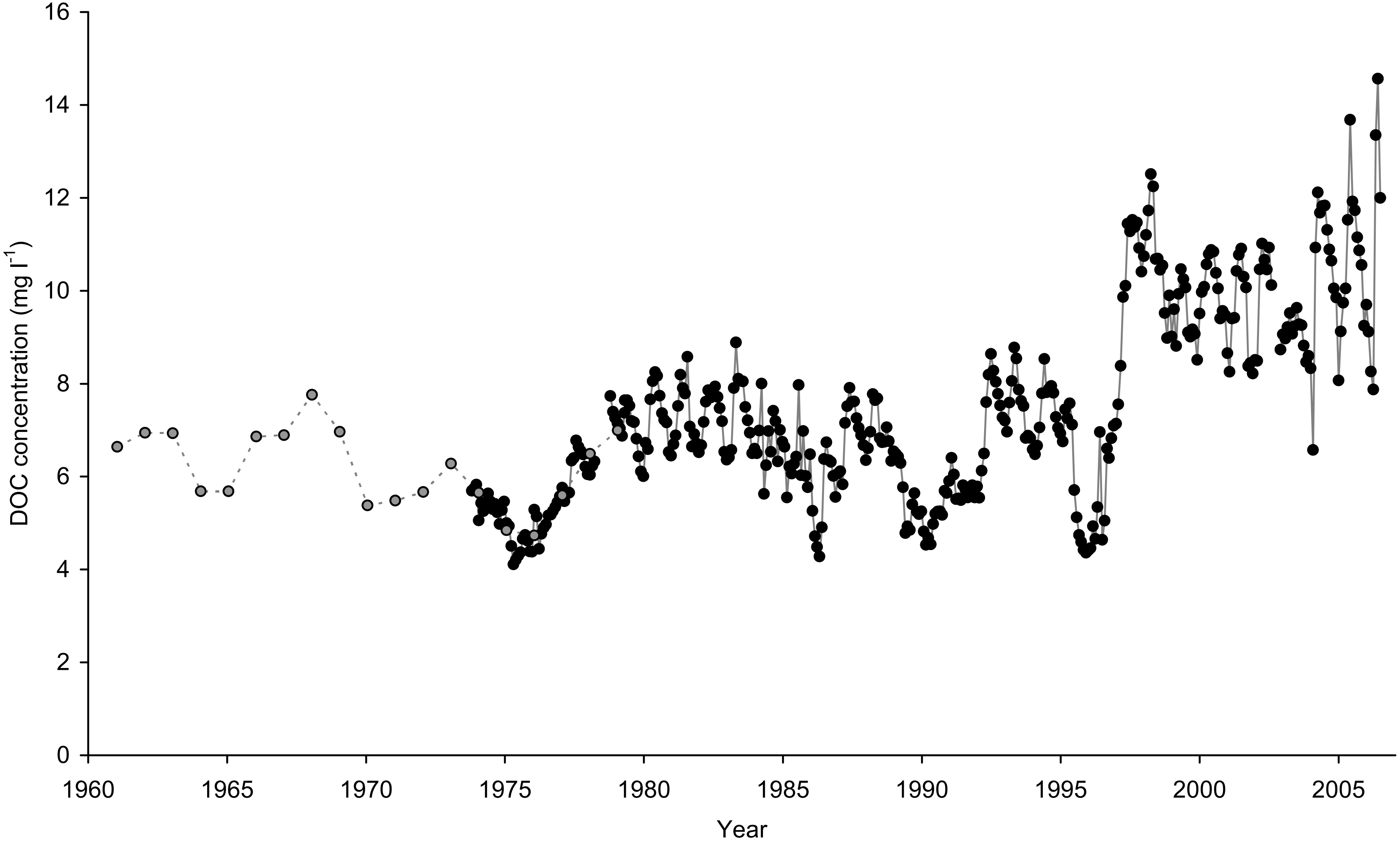


Figure 7.3.5. Monthly mean DOC concentration in water sampled at Langsett WTW (solid circle; grey circle shows annual mean data).

Table 7.3.1. Trends in DOC concentration, rainfall, temperature and wet deposited SO_4^{2-} identified by seasonal Kendall test.

	Median change *	*p*	Increase †
DOC 1990-2005			
Agden	+0.20	<0.001	53%
Broomhead	+0.30	<0.001	66%
Langsett	+0.33	<0.001	77%
Lower Laithe	+0.09	<0.001	18%
Keighley Moor	+0.33	<0.001	94%
DOC 1975-2005			
Agden	+0.08	<0.001	46%
Broomhead	+0.14	<0.001	75%
Langsett	+0.14	<0.001	73%
Rainfall			
All catchments		*ns*	
Temperature 1990-2005			
Emley Moor	+0.05	<0.01	0.75 ºC
Bingley	+0.05	<0.01	0.75 ºC
Temperature 1975-2005			
Emley Moor	+0.04	<0.001	1.2 ºC
Wet deposited SO_4^{2-}			
South group	-32.04	<0.001	-51%
North group	-29.76	<0.001	-38%

* changes in DOC measured in mg l^{-1} yr^{-1}; SO_4^{2-} measured in mg m^{-2} yr^{-1}
† % increase in relation to mean value in first five years of measurement

7.3.2. Climate and acid deposition effects on DOC concentration

Rainfall

No significant trends in annual rainfall were identified over either study area. In addition, no significant relationships between annual rainfall and DOC concentration were identified.

Temperature

A significant (p<0.01) increasing trend in mean monthly air temperature was identified in temperature records for both catchment groups for the period 1990-2005. The magnitude of the trend identified over both groups was 0.05ºC yr^{-1}, representing an increase in mean temperatures of 0.75ºC over the 15 year period (Table 7.3.1). A significant (p<0.05) relationship between annual mean temperature and DOC concentration was identified in the three catchments in the southern catchment group (r^2=0.22-0.26; Table 7.3.2). This relationship was identified as stronger in regression of annual temperature lagged by three years against DOC (r^2=0.28-0.31; Table 7.3.2). This lagged relationship was identified in four of the five catchments examined.

Table 7.3.2. Relationships identified between DOC concentration and annual mean temperatures for all catchments for the period 1986-2005.

1986-2005	Slope	r^2	*p*	d.f.
Lag = 0				
Agden	+0.98	0.25	0.018	18
Broomhead	+1.40	0.22	0.028	17
Langsett	+1.77	0.26	0.016	18
Lower Laithe		*ns*		
Keighley Moor		*ns*		
Lag = 1				
Agden	+0.78	0.16	0.048	18
Broomhead			*ns*	
Langsett			*ns*	
Lower Laithe			*ns*	
Keighley Moor			*ns*	
Lag = 2				
All catchments			*ns*	
Lag = 3				
Agden	+1.07	0.30	0.009	18
Broomhead	+1.62	0.31	0.01	17
Langsett	+1.85	0.28	0.011	18
Lower Laithe	+0.63	0.29	0.049	10
Keighley Moor			*ns*	

In the longer-term temperature record for the southern catchment group, a highly significant (p<0.001) increasing trend in annual temperature was identified. Trend magnitude was 0.04°C yr^{-1}, suggesting an increase of 1.2°C over the 30 year period. In all three catchments examined, all annual temperature factors tested in regression, including the three lag periods, were identified as being significantly related to DOC concentration (Table 7.3.3). The strongest relationship identified by regression was between annual temperatures lagged by a period of three years and DOC concentration (r^2=0.21-0.26).

Table 7.3.3. Relationships identified between DOC concentration and annual mean temperatures for Agden, Broomhead and Midhope catchments for the period 1962-2005.

1962-2005	Slope	r^2	*p*	d.f.
Lag = 0				
Agden	+0.81	0.25	<0.001	42
Broomhead	+1.27	0.24	0.001	41
Langsett	+1.25	0.21	0.001	42
Lag = 1				
Agden	+0.70	0.18	0.003	41
Broomhead	+1.14	0.17	0.004	40
Langsett	+1.10	0.15	0.007	41
Lag = 2				
Agden	+0.63	0.14	0.009	40
Broomhead	+1.06	0.14	0.009	39
Langsett	+1.08	0.14	0.010	40
Lag = 3				
Agden	+0.89	0.26	<0.001	39
Broomhead	+1.43	0.28	<0.001	38
Langsett	+1.34	0.21	0.002	39

Acid deposition

Highly significant (p<0.001) decreasing trends in wet deposited sulphate were identified over both southern (32.04 mg m^{-2} yr^{-1}) and northern (29.75 mg m^{-2} yr^{-1}) catchment groups for the period 1990-2005. Significant (p<0.05) relationships between wet deposited sulphate and DOC concentration were identified in four of the five catchments (r^2=0.21-0.31; Table 7.3.4).

Table 7.3.4. Relationship between wet deposited SO_4^{2-} and DOC concentration 1986-2005.

	Slope	r^2	*p*	d.f.
Agden	-0.0026	0.31	0.008	18
Broomhead	-0.0037	0.21	0.033	17
Langsett	-0.0041	0.22	0.024	18
Lower Laithe			*ns*	
Keighley Moor	-0.0046	0.31	0.028	12

Accumulative effects of extrinsic factors on DOC

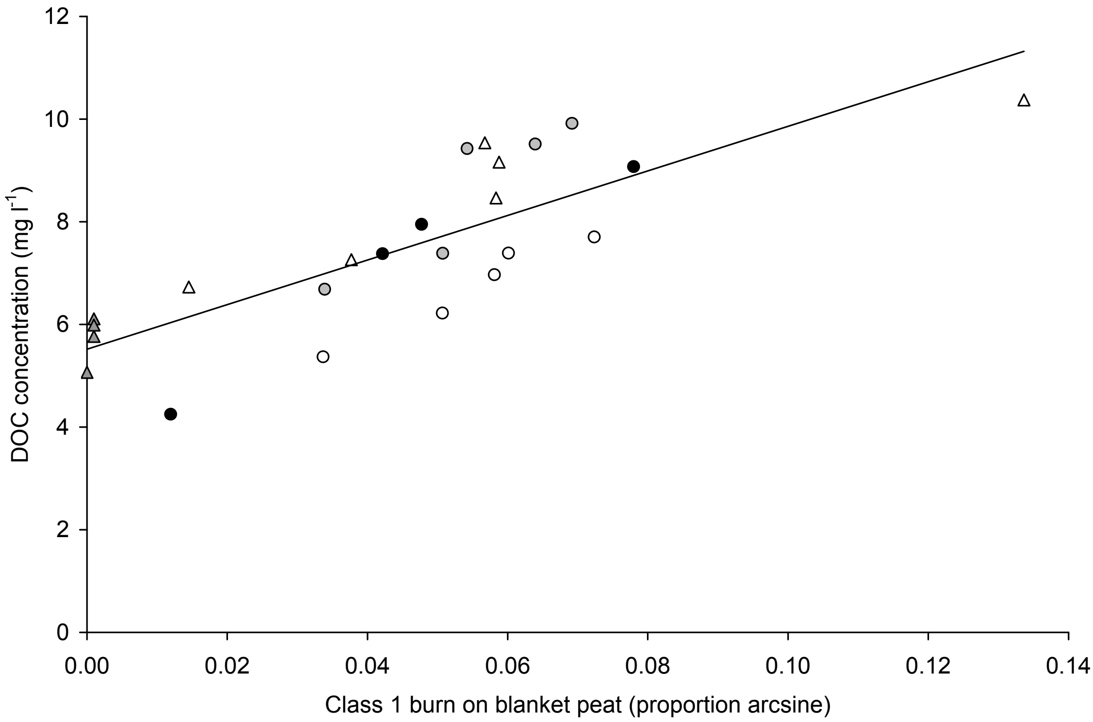
For three of the five catchments, multiple regression selected mean annual temperatures lagged by a period of three years as the only significant factor related to changes in DOC concentrations (r^2=0.28-0.31; Table 7.3.5). Annual wet deposited sulphate was selected for the other two catchments, and in only one catchment, annual rainfall was added to the regression model, improving the degree of variance explained from r^2=0.31-0.54.

Table 7.3.5. Results of stepwise multiple regression for DOC concentration.

	Factor	r^2	*p*	Factor 2	r^2	*p*	d.f.
Agden	SO_4^{2-}	0.31	0.008	Rain -0	0.54	0.006	18
Broomhead	Ann T -3	0.31	0.010	*none*			17
Langsett	Ann T -3	0.28	0.011	*none*			18
Lower Laithe	Ann T -3	0.29	0.049	*none*			10
Keighley Moor	SO_4^{2-}	0.31	0.028	*none*			12

7.3.3. Changes in land use/management and DOC concentration

Of the land use/soil combination factors tested in forward-entry multiple regression using three month mean DOC for all catchments, the only factor identified was the proportion of Class 1 burn on blanket peat (r^2=0.58, p<0.001, n=24; Figure 7.3.6 top). This relationship was again identified using calendar year mean DOC concentration (r^2=0.52, p<0.001, n=22; Figure 7.3.6 bottom).



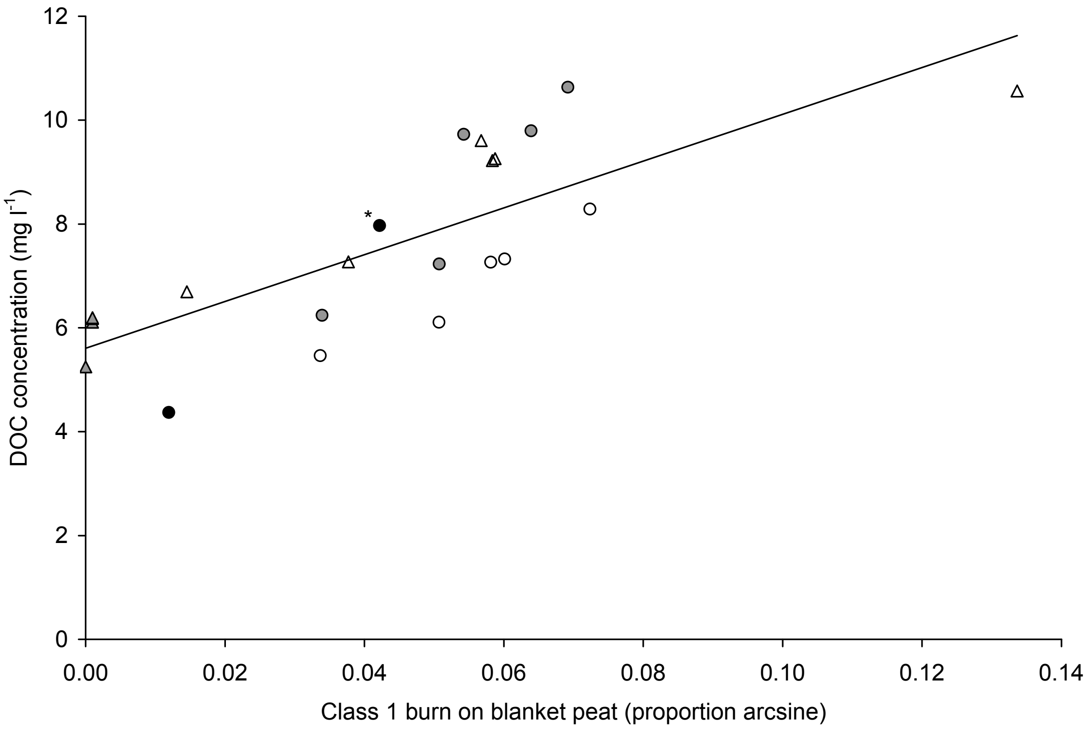


Figure 7.3.6. Proportion of catchment as Class 1 burn against annual mean DOC concentration for all study catchments (1989-2005). *Top*: Feb, Apr, Jun mean (r^2=0.58, p<0.001); *Bottom*: calendar year mean (r^2=0.52, p<0.001) * KM 1999 mean based on Sept 1998 – Aug 1999.

Symbols represent Agden (open circle), Broomhead (open triangle), Langsett (grey circle), Lower Laithe (grey triangle), Keighley Moor (black circle).

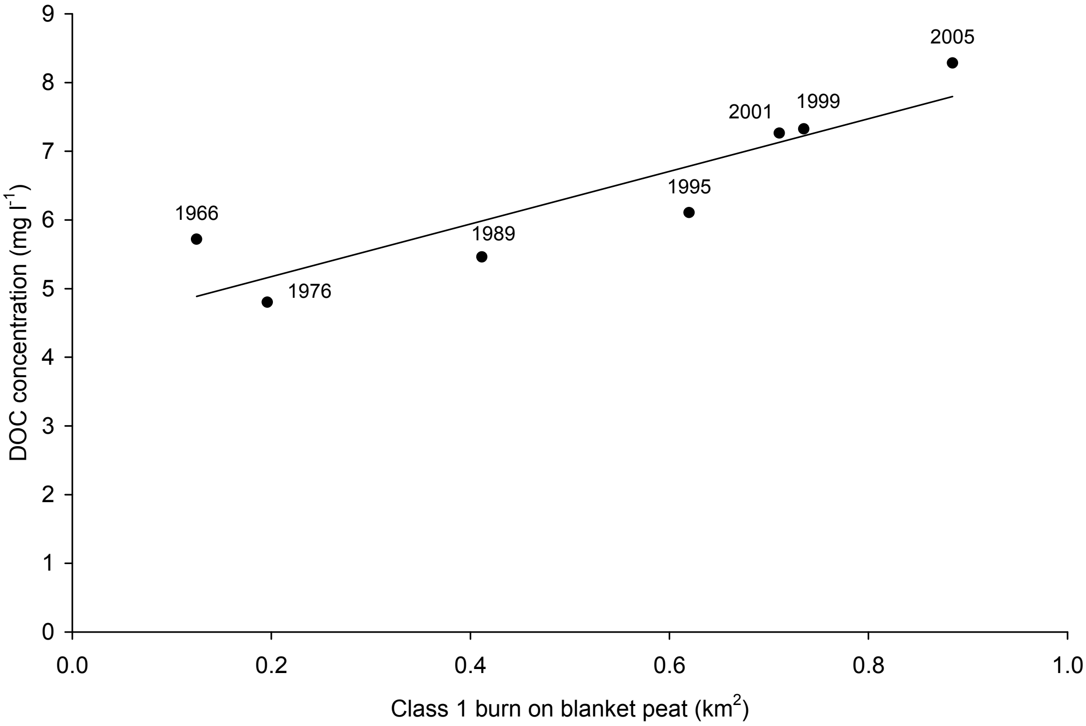
For the period 1989-2005, significant relationships between the area of Class 1 burn on blanket peat and DOC concentration were identified in each catchment explaining a high degree of variance in DOC (r^2=0.68-0.92; Table 7.3.6; Figures 7.3.7-7.3.11). The relationship was also significant for the three catchments examined over the longer-term period 1966-2005. The degree of variance in DOC explained by Class 1 burn on blanket peat remained high over this period (r^2=0.67-0.92), except in Langsett where this reduced to r^2=0.48, owing to a very high estimated value of DOC for 1968 (Figure 7.3.9a).

Table 7.3.6. Relationship between area of Class 1 burn and DOC concentration determined in all catchments over period of study.

	Slope	r^2	*p*	d.f.
1989-2005				
Agden	+6.20	0.92	0.006	4
Broomhead	+1.49	0.68	0.027	5
Langsett	+7.18	0.81	0.025	4
*Lower Laithe **	*+185.69*	*0.98*	*0.007*	*3*
Keighley Moor	+45.33	0.88	0.015	3
1976-2005				
Agden	+5.09	0.92	0.002	5
Broomhead	+2.02	0.67	0.016	6
Langsett	+6.18	0.88	0.003	5
1966-2005				
Agden	+3.83	0.75	0.007	6
Broomhead	+1.93	0.70	0.006	7
Langsett	+3.13	0.48	0.050	6

* For Lower Laithe, where three of the four observations are almost identical, regression is not an appropriate statistical test. Regression model is therefore not shown on Figure 7.3.10.

a)



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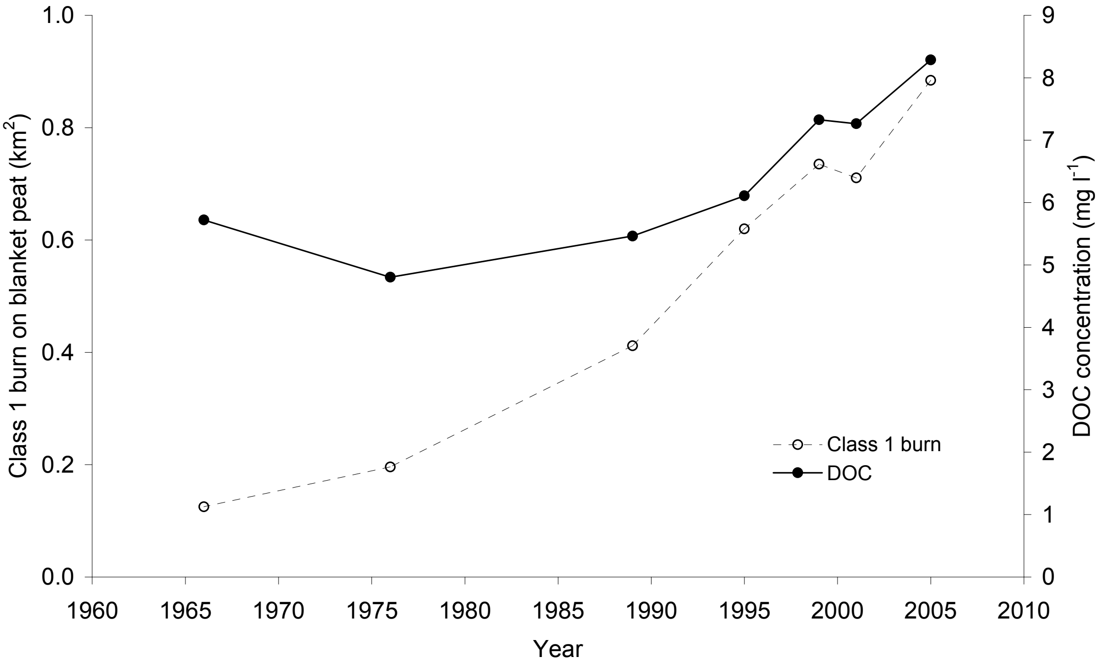
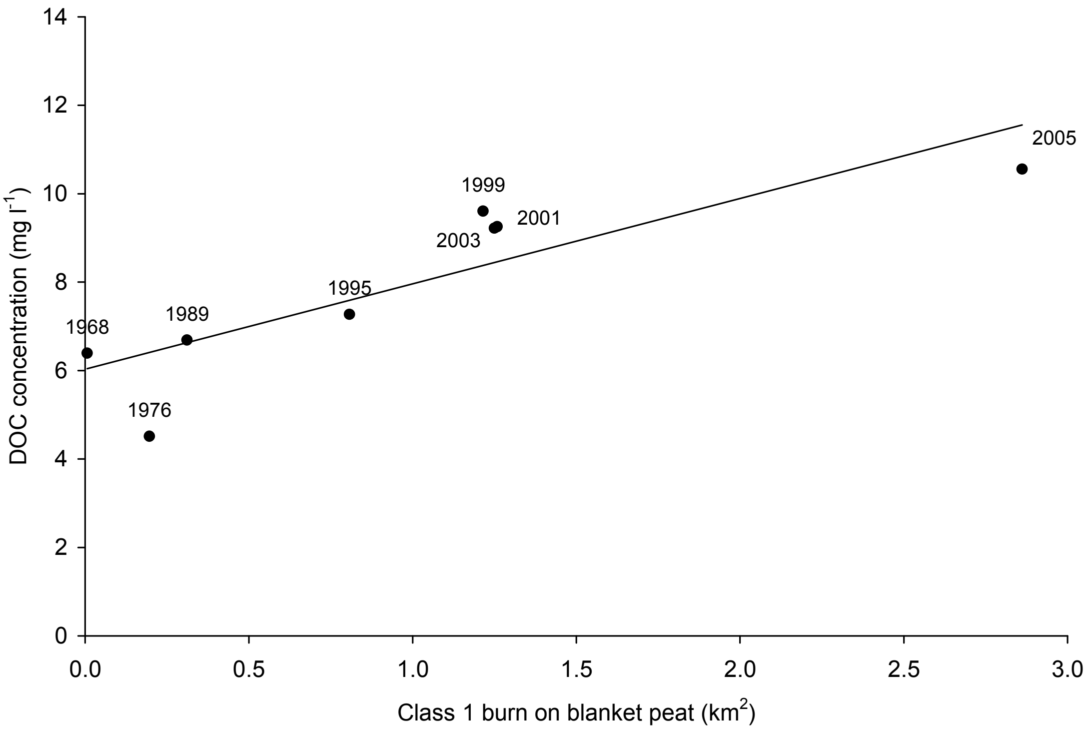


Figure 7.3.7. Relationship between area of Class 1 burn and annual mean DOC concentration in drainage for Agden (1966-2005). a) Class 1 burn against annual mean DOC (r^2=0.75, *p*=0.007); b) Increasing trend in DOC and change in area of Class 1 burn.

a)



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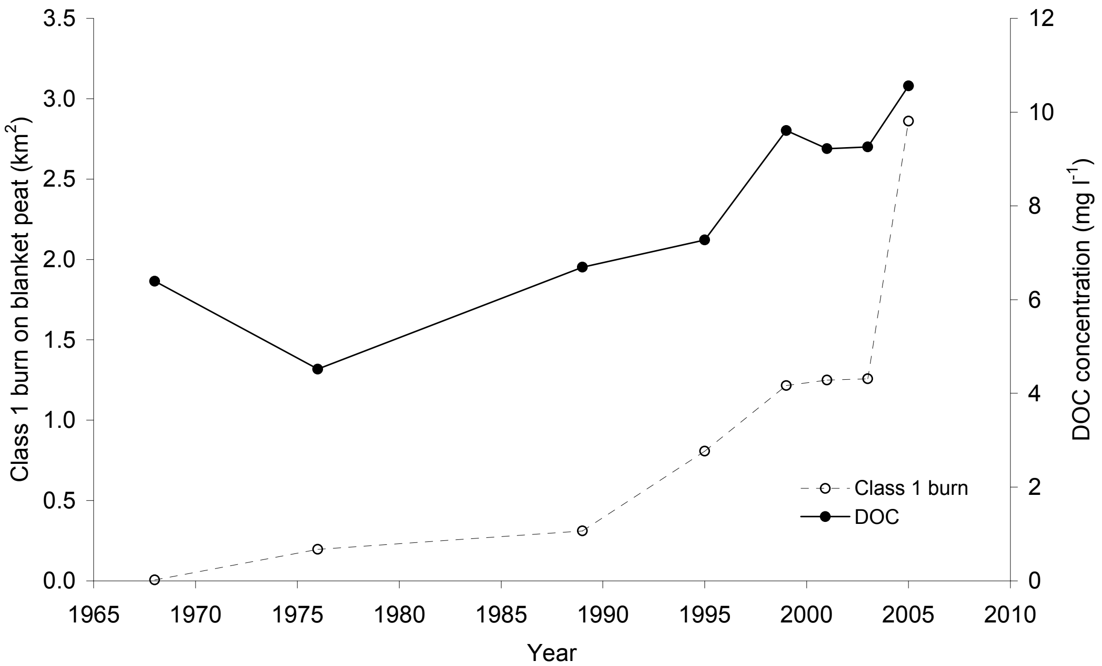
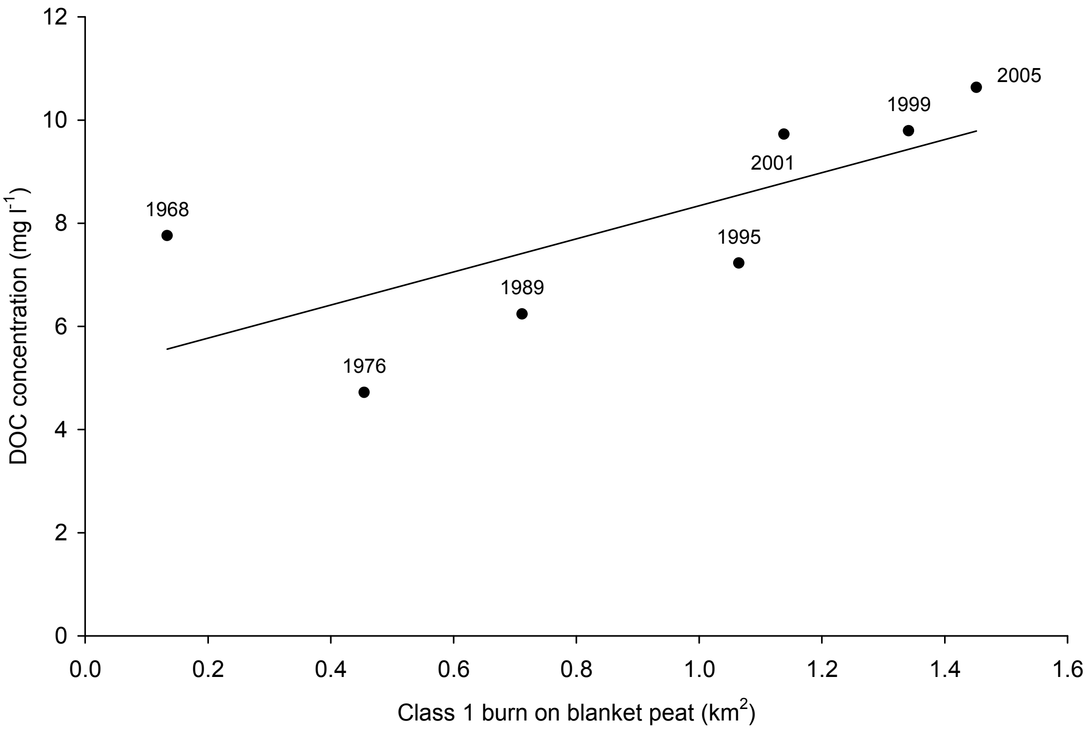


Figure 7.3.8. Relationship between area of Class 1 burn and annual mean DOC concentration in drainage for Broomhead (1968-2005). a) Class 1 burn against annual mean DOC (r^2=0.70, *p*=0.006); b) Increasing trend in DOC and change in area of Class 1 burn.

a)



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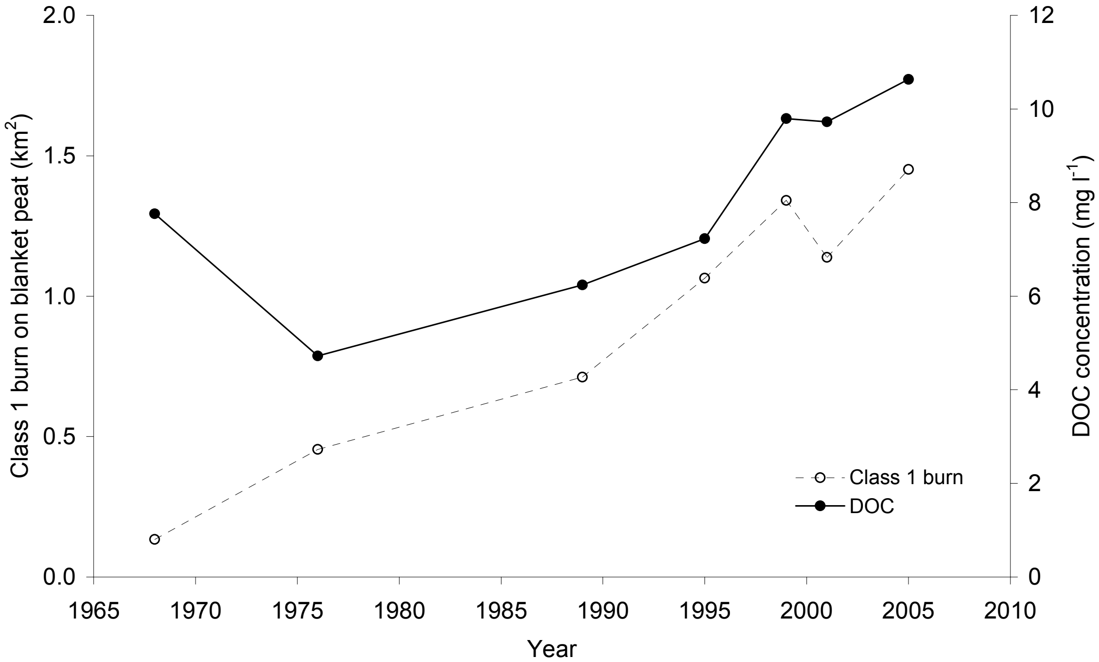
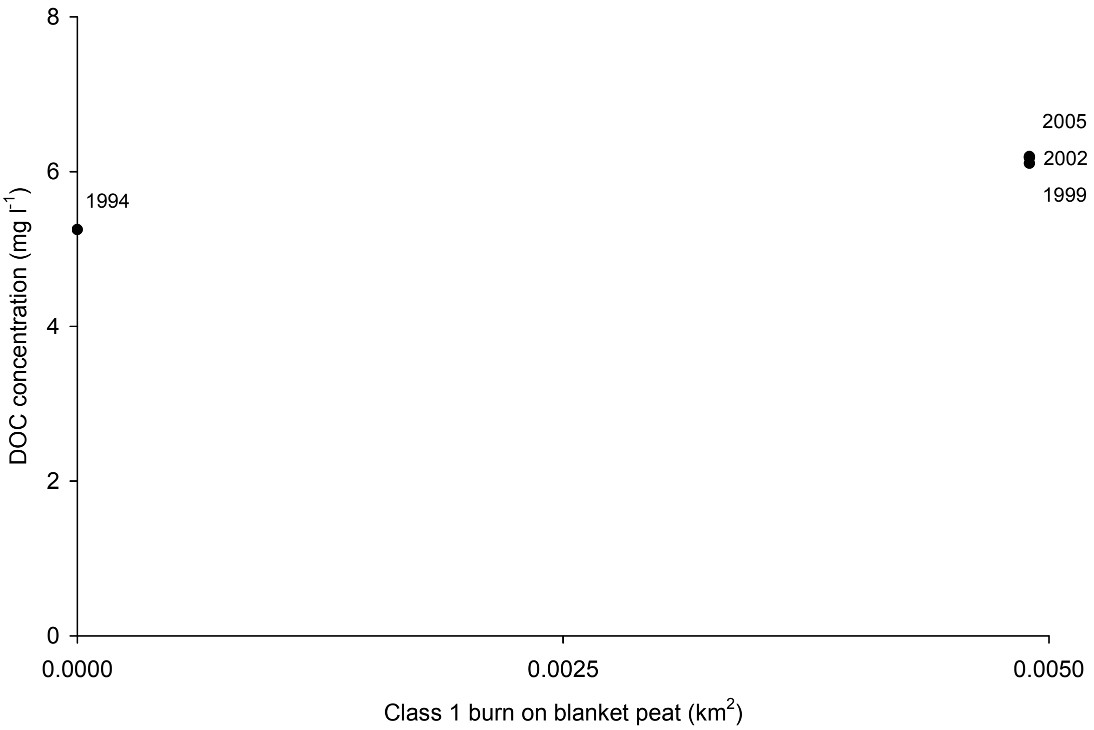


Figure 7.3.9. Relationship between area of Class 1 burn and annual mean DOC concentration in drainage for Langsett (1968-2005). a) Class 1 burn against annual mean DOC (r^2=0.48, *p*=0.05); b) Increasing trend in DOC and change in area of Class 1 burn.

a)



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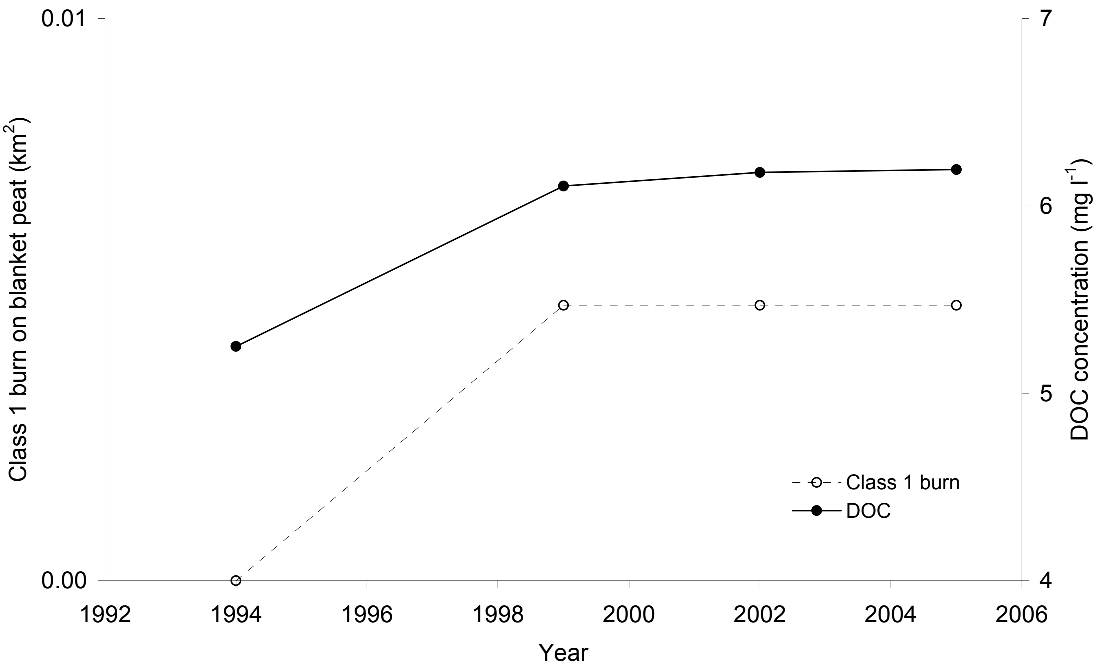
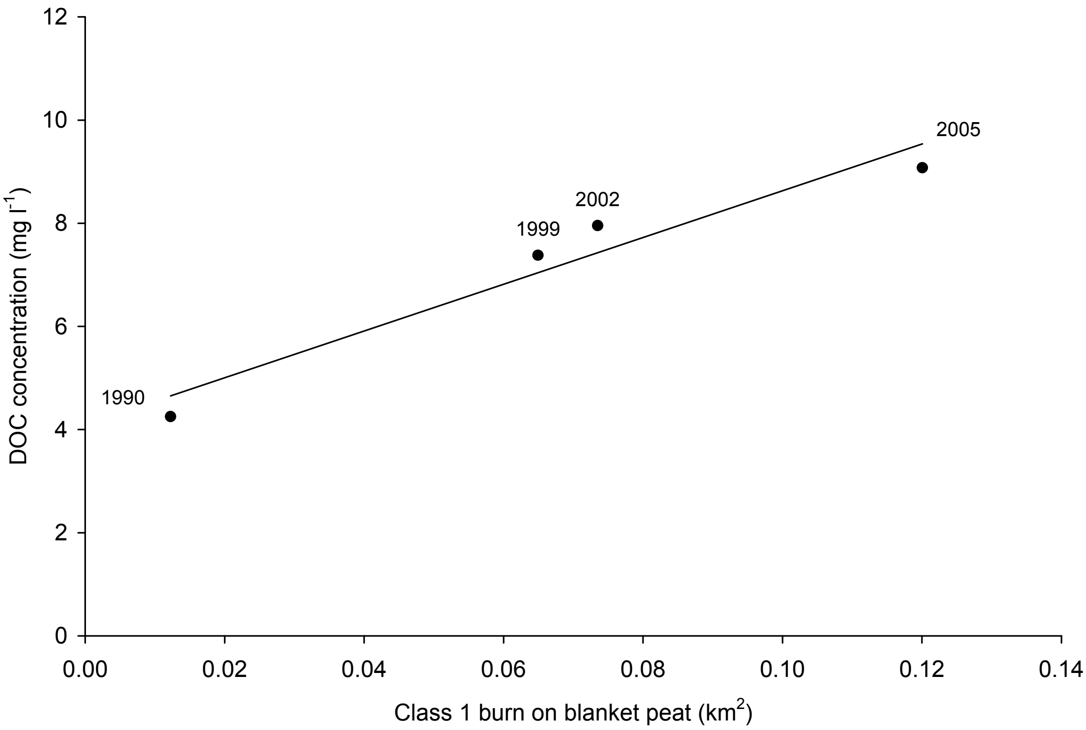


Figure 7.3.10. Relationship between area of Class 1 burn and annual mean DOC concentration in drainage for Lower Laithe (1994-2005). a) Class 1 burn against annual mean DOC (regression model not shown); b) Increasing trend in DOC and change in area of Class 1 burn.

a)



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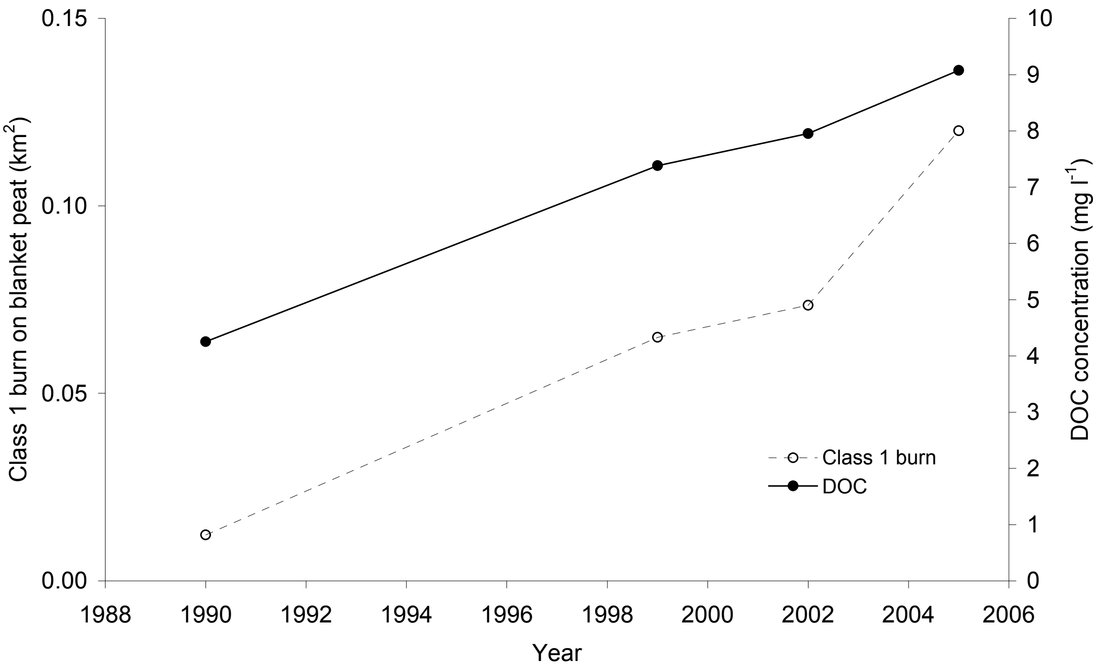

Figure 7.3.11. Relationship between area of Class 1 burn and annual mean DOC concentration in drainage for Keighley Moor (1990-2005). a) Class 1 burn against annual mean DOC (r^2=0.88, *p*=0.041); b) Increasing trend in DOC and change in area of Class 1 burn.

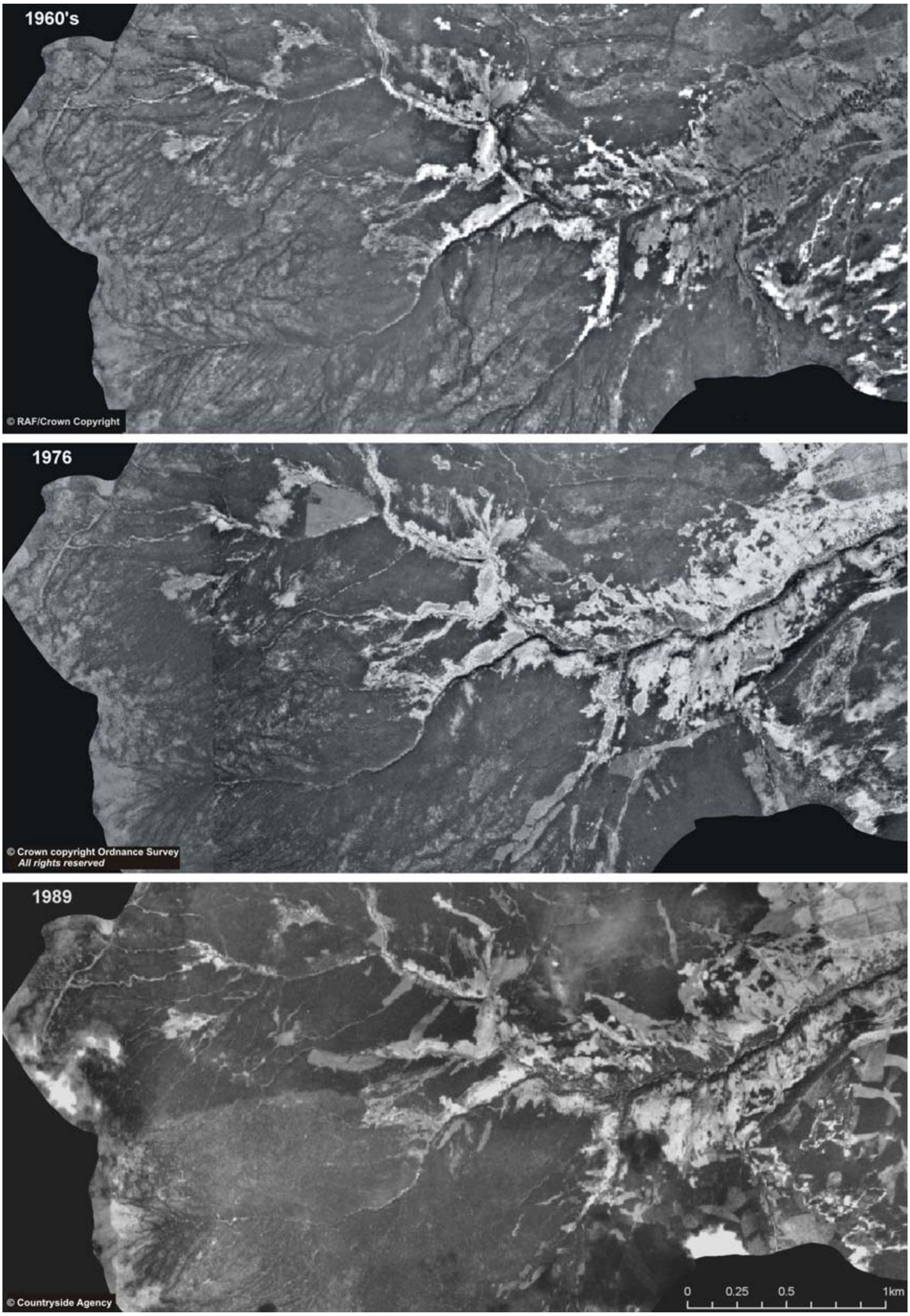

Figure 7.3.12. Changes in the extent of burn management on blanket peat moorland over four decades. Large bright irregular area in the centre of image is a large stand of bracken.

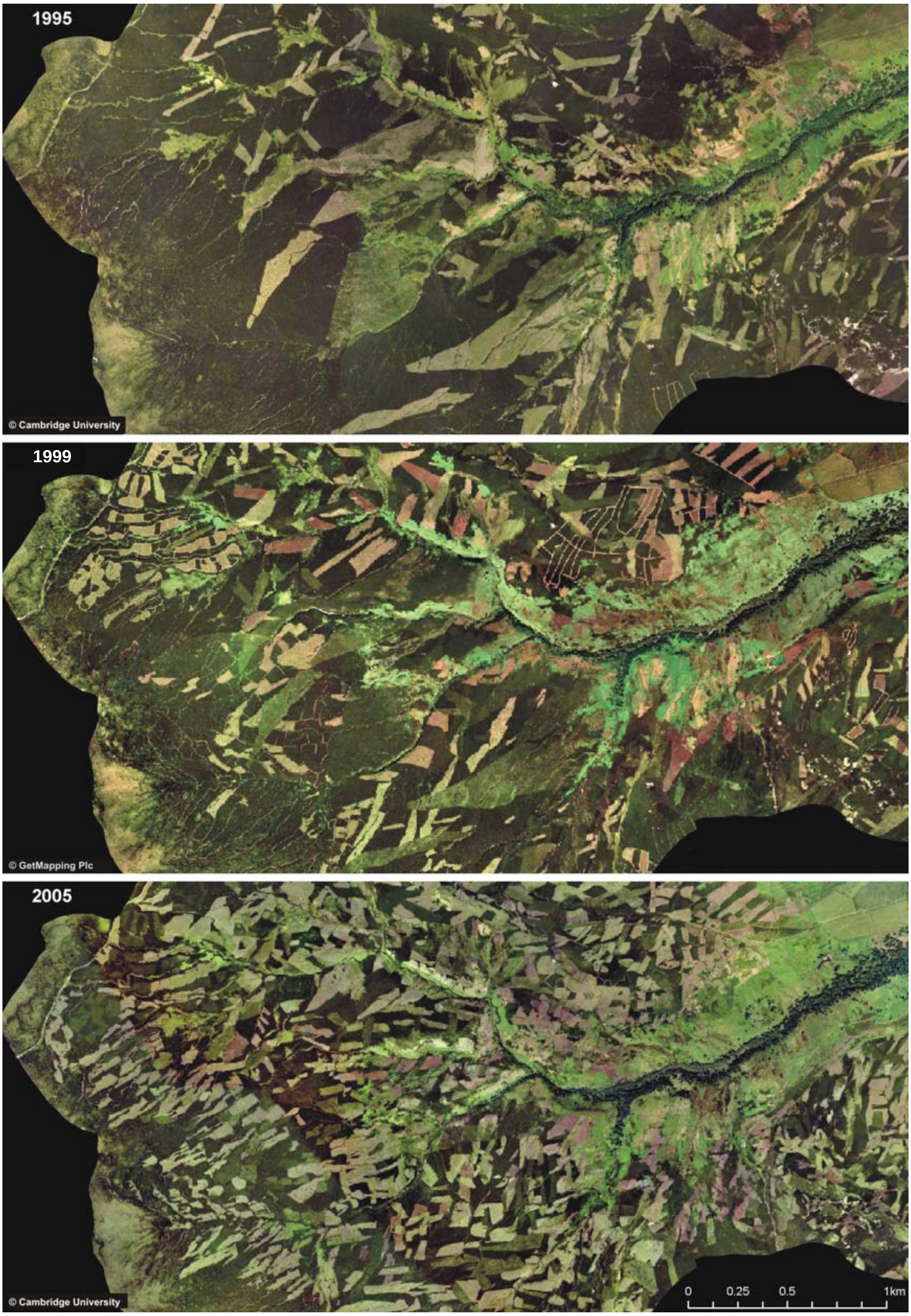

Figure 7.3.12 cont. Changes in the extent of burn management on blanket peat moorland over four decades.

7.4. Discussion

This study examined the effects of both extrinsic and intrinsic factors on drainage DOC concentration from five upland peat catchments in two areas of the South Pennines. Over the period of study, it is reasonable to assume that there was no change within each catchment for the intrinsic factors previously shown to influence drainage DOC (i.e. percent cover of blanket peat (e.g. McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001), slope (Aitkenhead *et al*., 1999; Eckhardt and Moore, 1990), altitude (Hope *et al*. 1997a) or drainage (Eckhardt and Moore, 1990)). It is also reasonable to assume that extrinsic factors will have the same influence over catchments located within the same catchment group owing to their geographical proximity (<5 km). The analysis presented here could therefore be considered as essentially a reconstruction of a controlled experiment, thereby allowing the effects of extrinsic factors and changes in land management to be examined.

Water colour was used to provide data on changes in DOC concentration in catchment drainage over the period of study. The humic fraction of DOC has particular significance in the context of long-term DOC records, as anthropogenic input of DOC from sewage (e.g. Eatherall *et al*., 2000) and industrial (e.g. Tipping *et al*., 1997) point-source effluents, products of plant decomposition from early stages of decay (e.g. Palmer *et al*., 2001) and atmospheric deposition of DOC in rain (e.g. Worrall *et al*., 2003a) could provide further contribution of non-humic fractions to overall DOC concentrations. Although the relationship between colour and DOC varies seasonally (e.g. Wallage *et al*., 2006) and between years (e.g. Hongve *et al*., 2004), determination of the humic fraction of DOC 'hDOC' from water colour may serve as the best long-term indicator of DOC derived from peat decomposition and therefore provide evidence for loss of 'old' carbon i.e. depletion of long-term carbon storage. The decomposition processes in blanket peat that are responsible for these DOC products are primarily driven by microbial activity and are controlled by a combination of factors including soil moisture, temperature, pH and peat structure (McDonald *et al.*, 1991). Some of these factors have been directly assessed here.

Rainfall could have a positive affect on drainage DOC concentration in several ways. During periods of increased rainfall, DOC concentrations in surface waters could increase as a result of changes in discharge (e.g. Grieve, 1984, 1991; Tranvik and Jansson, 2002). Conversely, following periods of high soil moisture deficit (as a result of low rainfall), increases in water colour have also been observed (e.g. Naden and McDonald, 1989). This could implicate increased microbial decomposition, as rapid peaks in microbial activity have been shown to follow rewetting of dried organic matter (Birch, 1958; 1959). Over both time periods of analysis (1986-2005 and 1962-2005), however, no trends in rainfall or significant relationships with annual rainfall amounts in the year of DOC measurement were identified. These observations suggest that the increases in DOC noted in this study are unlikely to merely relate to changes in discharge (see also Chapter 8).

That no lagged rainfall factor was identified here as a significant predictor for measured drainage DOC does not infer that antecedent conditions, controlled in part by precipitation, are not linked with the changes in DOC observed. It must be noted that rainfall only provides a weak indicator of soil moisture (Evans *et al.*, 2005). In shorter-term datasets, however, both soil moisture and rainfall have been related to peaks in colour release from peat catchments (Naden and McDonald, 1989). Deviations from the general trend of drainage/reservoir water DOC concentrations between 1995 and 1998 are evident in the DOC time-series derived for all five catchments examined here (Figures 7.3.1-7.3.5). Reduced water colour in drainage immediately following periods of drought and increasing trends in colour for 3-4 years after the 'event' have been observed in a number of catchments in the South Pennines (e.g. Watts *et al*., 2001). This response of colour levels to drought events has been ascribed to a initial resistance of peat to rewetting, as a result of hydrophobic molecular arrangement (Hayes, 1987), which delays access to the 'store' of colour produced during water table drawdown (Mitchell and McDonald, 1992). Although the influence of drought events on DOC production appears important for all catchments in this study, it does not explain differences in the trend of DOC concentrations after 1998. In four of the catchments examined here (Agden, Broomhead, Langsett and Keighley Moor), DOC concentrations are still increasing in 2005/6 (Figures 7.3.2-7.3.5), yet in Lower Laithe there appears to be no significant increase in DOC since 1998 (Figures 7.3.1 and 7.3.10).

Positive relationships between temperature and DOC production have been observed before in both experimental peat cores (e.g. Freeman *et al*., 2001a) and in field-based studies (e.g. Tipping *et al*., 1999). These observations, combined with temperature increases observed in some upland locations (e.g. Holden and Adamson, 2002), have led to suggestions that the increases in DOC release observed recently are partly driven by temperature changes. This is quantified by Evans *et al*. (2006) who propose a 10-20% rise in DOC concentrations from an increase in mean summer temperature of around 0.66ºC in the 1990s. Worrall *et al*. (2004b) also produce evidence to support this proposal and demonstrate a 12% increase from a 0.78ºC change since the 1970s. The 0.75ºC rise in mean annual temperature determined in this study (1990-2005) accounted for between 28-31% of the variance in DOC concentration within four of the five catchments examined. The range in degree of variance explained in these four catchments is remarkably small (i.e. 4%). In these four catchments, DOC concentrations were estimated to increase by between 18-77% compared to 1990-1994 mean concentrations. These figures suggest that over this period the temperature increase was responsible for between 5-20% rise in DOC in these catchments. This is consistent with estimates from other studies (Worrall *et al*., 2004b; Evans *et al*., 2006), and provides further evidence that the effects of climate change are important drivers of the observed DOC increase over the recent past.

It should be noted though that the increases in temperature determined in this study fall far short of those experimentally demonstrated to produce the scale of increase in DOC observed more widely in the UK (Freeman *et al*., 2004) and in the fifth catchment examined here, where the largest increase in DOC concentration was estimated (94%), no relationship with temperature was identified. This indicates that further factors must also be involved. The mobility of organic acids (including DOC) is inversely related to mineral acidity (e.g. Krug and Frink, 1983) and ionic strength (e.g. Tipping and Hurley, 1988). During drought conditions, the production of SO_4^{2-} following oxidation of sulphur stored in peat, with a concomitant increase in ionic strength, was associated with reductions in interstitial DOC concentration (Clark *et al*., 2005). Sulphur emissions in the UK reduced by 89% between 1970 and 2005 (NAEI, 2007), as is evident in the significant declining trend in wet deposited SO_4^{2-} determined in this study (Table 7.3.1). Such observations prompted suggestions that recovery from acid deposition could lie behind the recent upward trends observed in DOC (e.g. Evans *et al.*, 2005; 2006; Vuorenmaa *et al.*, 2006).

Decreasing trends in wet deposited SO_4^{2-} of between 30-32 mg m^{-2} $year^{-1}$ were identified in the data sourced from the ADMN monitoring stations, and in four of the study catchments changes in deposited SO_4^{2-} were significantly related to DOC concentrations, explaining between 21-31% of the observed variance over the studied period. This explained variance is of the same magnitude as that seen for temperature over the same period (r^2=0.28-0.31) for the catchments where a relationship with SO_4^{2-} was identified. Multiple regression did not however identify any cumulative link between temperature and SO_4^{2-} factors in any of the five catchments examined. That no relationship between sulphate deposition and DOC concentration was identified for Lower Laithe (less than 5 km to the south of Keighley Moor where changes in SO_4^{2-} explained 31% of the variance in DOC) is consistent with other studies demonstrating that artificial catchment acidification (Lydersen *et al.*, 1996) and catchment scale acid-exclusion experiments (Wright *et al.*, 1993) had no significant effect on DOC concentrations. The evidence presented here indicates that changes in SO_4^{2-} deposition over the period 1986-2005 correlate with changes in DOC concentration in four of the five study catchments where DOC concentrations are continuing to increase. Negative correlations between SO_4^{2-} and DOC in other studies have been suggested to relate to underlying changes in hydrology (Eimers *et al.*, 2008). DOC increases have also occurred in some areas of the UK affected by very low levels or no acid deposition (Evans *et al*., 2005).

The increase in burning in four of the study catchments (Table 7.2.3) and in particular its expansion into areas of blanket peat since the 1960s (e.g. Figure 7.3.12) is striking, as is the highly significant relationship between the proportion of Class 1 burn on blanket peat and DOC concentration across all catchments ($r^2=0.58$, $p<0.001$). This interaction is significantly stronger in each individual catchment, where increases in the area of burn explain 70-98% of the increases in DOC, except in Langsett where a very high estimate of DOC in 1968 reduces this to 48%. The latter may result from the determination of colour on unfiltered samples in early data (Watts *et al*., 2001) or may arise for other reasons. The regression of burning and DOC in Lower Laithe which explains 98% of the variance there (Figure 7.2.10) may be providing a false identification of a relationship due to the low number of observations. However, despite the potential error, as highlighted by Figure 7.3.10, it is evident that from 1999 to 2005 there was no increase in burning and no significant increase in annual DOC at Lower Laithe.

At present there are no studies providing experimental evidence of the effect of controlled burning on carbon dynamics in peat. Several studies (e.g. Ward *et al*., 2007; Worrall *et al*., 2007; Clay *et al*., 2009) have examined interactions between burning and water quality in the UK, but do not provide comparable analysis for several reasons. Two of these studies have focussed on burn patches at the end of burn cycles i.e. 9-10 years old when vegetation has almost fully recovered (e.g. Worrall *et al*., 2007; Ward *et* *al*., 2007). Studies that have monitored burns immediately following burning (e.g. Clay *et al*., 2009) have measured DOC concentrations in soil water and surface water runoff, not drainage as measured here, and recognise that these parameters do not allow inference of any changes in drainage at catchment scale. It is therefore not possible to make comparisons to these studies; however this is addressed in Chapter 9.

7.5. Conclusion

No single factor has been proposed that explains the increasing trends in UK drainage DOC concentrations in other work. This study has examined several extrinsic and intrinsic factors in isolation and identified significant relationships between temperature, sulphate deposition and controlled burning factors and DOC concentration. Annual variability in climate and acid-deposition factors explain the same degree of variance in some but not all catchments. The only factor identified consistently in all catchments was the area of Class 1 burn on blanket peat, and on its own explained more than twice the degree of variance in DOC concentrations than other tested factors.

The data in this chapter provides evidence of the role of localised factors in controlling DOC production in blanket peat and may help explain larger increases observed in the UK than elsewhere (Skjelkvåle *et al*., 2005) or why other drivers cannot explain the same degree of variance in the UK as in other regions (Monteith *et al*., 2007). Lower Laithe in effect provides a control catchment for burning in this study, and clearly shows that for catchments where no change in the area of burning on blanket peat was detected, there was no significant change in DOC concentration.

Inclusion of rainfall within the analyses presented here indicates that the increases in DOC concentration are unlikely to be controlled by changes in precipitation and runoff. Other studies have shown that increases in DOC flux in catchment drainage have occurred over the same period as the increases in DOC concentration have been observed. There is however a requirement to consider the flux of carbon released as DOC from upland peat, to provide a better understanding of the mechanisms behind drivers of changes in concentrations. This will be addressed in Chapter 8.

This chapter provides a valuable contribution to studies of long-term changes in DOC concentrations in the UK. In addition to the evidence presented in Chapters 5 and 6, the data here suggest that current levels of DOC in surface waters have been significantly increased by changes in land management policy. This has consequence for utility companies and national carbon budgets.

Chapter 8: Influence of land management on DOC efflux from upland peat soils

8.1. Introduction

Humic DOC (hDOC) concentrations in drainage waters for the five South Pennine reservoir catchments examined in Chapter 7 were found to have increased between 18% and 94% for the period 1990-2005 as a consequence of average temperature rise, reductions in sulphur deposition and, predominantly, increases in the extent of moorland burning on blanket peat. Together with the data presented in Chapters 5 and 6, this provides strong evidence for negative effects arising from controlled moorland burning on carbon dynamics in these environments. This increasing presence of hDOC, the product of peat decomposition, in catchment drainage implies increased degradation of peat where managed vegetation burning is common.

That the changes observed for the catchments examined in Chapter 7 are of the same order of magnitude as increases in DOC concentration recorded for other upland peat catchments across the UK (Freeman *et al*., 2001a; Evans *et al*., 2005), suggests this is a widespread phenomenon, and could therefore indicate a significant loss of carbon from upland peat nationally. However, DOC concentrations do not directly provide evidence for the actual scale of carbon loss as they are affected by changes in catchment discharge (e.g. Grieve, 1984; Tranvik and Jansson, 2002). A number of studies have quantified DOC export in rivers around the world (see Hope *et al*., 1994; Dawson and Smith, 2007) but very few have examined the actual flux associated with increasing DOC concentrations in the UK. Worrall *et al*. (2004a) estimated DOC flux for all UK rivers to be of the order of 0.86 Mt C for the year 2002, increasing at a rate of 0.02 Mt C yr^{-1}. These estimates do not, however, provide evidence for the origin of the DOC measured, and therefore the component of these figures that can be attributed to carbon losses from deep peat storage. Worrall *et al.* (2008) suggest increases from upland peat in the North Pennines of 0.6 t km^{-2} yr^{-1} since the 1970s.

DOC is recognised as a significant component of carbon budgets (Meybeck, 1993; Pastor *et al.*, 2003; Worrall *et al.*, 2003b; Billet *et al.*, 2004). Considering the significant role identified between the area of controlled burning on blanket peat and both spatial (Chapters 5 and 6) and temporal (Chapter 7) variation in hDOC concentrations, quantification of the carbon export that these changes in concentrations represent is key to understanding the overall carbon dynamics of upland peat environments. The aim of this chapter is therefore to determine hDOC flux for the five catchments examined in Chapter 7 to quantify the amount of carbon that is removed from them via fluvial pathways.

Stream flow data for surface waters draining the five study catchments were unfortunately not available and estimation of streamflow, often referred to as runoff (Ward and Robinson, 1986), for the period of DOC concentration data availability therefore required a data modelling approach. Rainfall-runoff modelling has a long history (Beven, 2001) and runoff in ungauged catchments is commonly modelled from the response observed in gauged catchments with matching physical characteristics (e.g. Sefton and Howarth, 1998; Kokkonen *et al.*, 2003). This approach was adopted here. Rainfall data were available for all catchments dating from 1961, and a rainfall-runoff model was developed. The objectives for this chapter were therefore defined as:

i. select a series of upland peat catchments in England and Wales where stream flow and rainfall is monitored;
ii. define physical characteristics that influence runoff for the selected 'model' and study catchments;
iii. identify those 'model' catchments where runoff behaviour might be expected to be comparable to the study catchments;
iv. calculate runoff:rainfall ratios for the selected catchments and use these ratios to model runoff response within the study catchments;
v. estimate DOC flux for the study catchments for the period of DOC concentration data availability;
vi. examine the influence of land management on carbon loss from upland peat.

8.2. Methods

8.2.1. Selection of upland peat catchments for runoff modelling

The locations of flow gauging stations on rivers and streams draining upland areas of England and Wales were initially obtained from the UK National River Flow Archive (NRFA; www.ceh.ac.uk/nrfa). National Soil Resource Institute (NSRI) digital soil data derived from Mackney *et al*. (1983) were then used to exclude flow gauge stations monitoring runoff for catchments that did not contain areas of raw peat soils (sub-groups 10.11-10.14; Avery, 1980). This subset was then further stratified by excluding catchments where natural flow regime is affected by water abstraction or storage within the catchment. This identified a set of 30 'model' catchments (Figure 8.2.1), for which monthly precipitation and daily flow gauge data were obtained from the NRFA. Drainage catchments for the selected flow gauge stations were derived using Ordnance

Survey PANORAMA 1:50 000 digital terrain models (DTMs) and the utilities within ArcHydro GIS tools (Maidment, 2002).

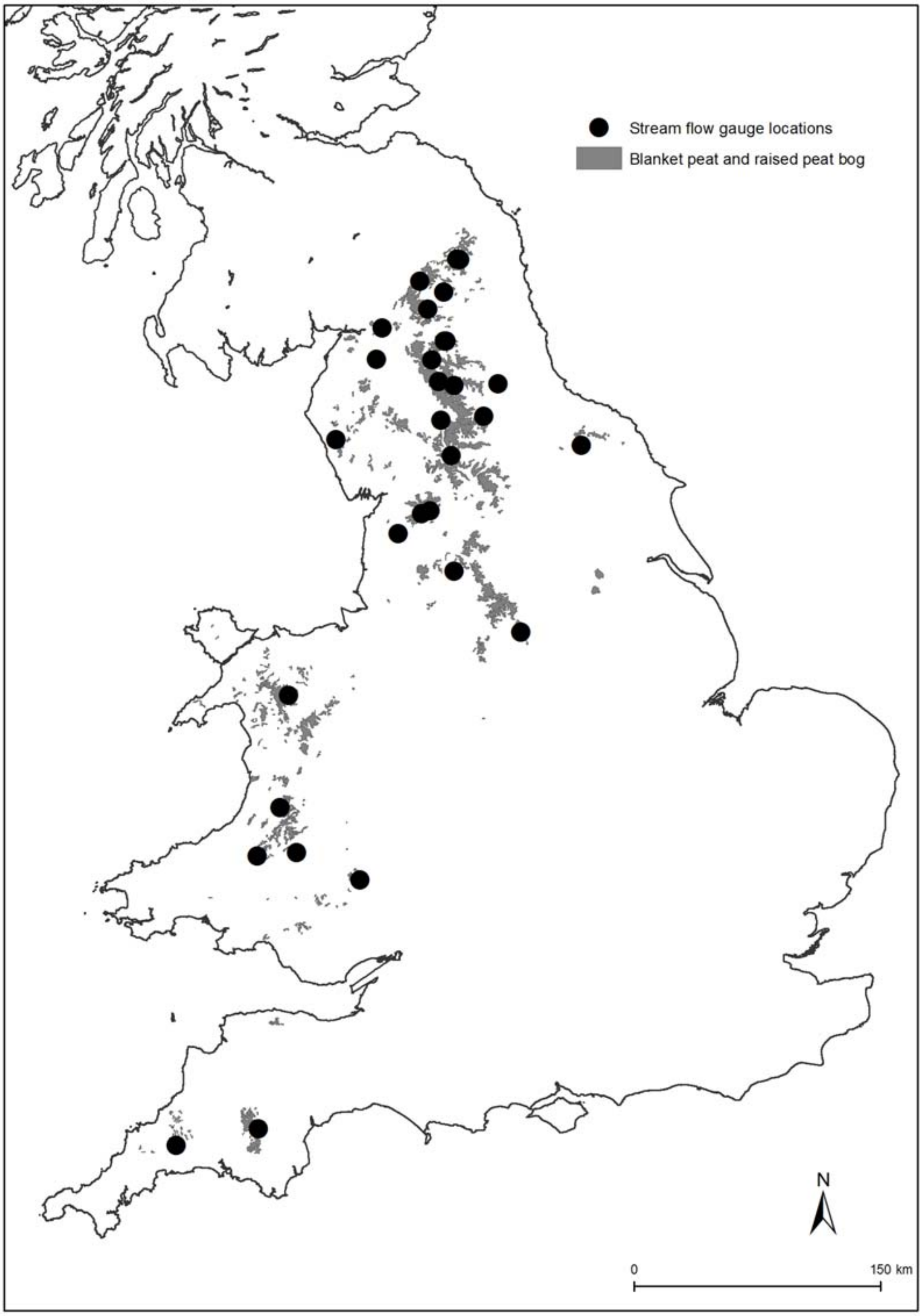

Figure 8.2.1. Location of stream flow gauges monitoring surface waters draining 30 upland peat catchments selected for runoff modelling.

8.2.2. Physical catchment descriptors

Sefton and Howarth (1998) propose four categories of physical catchment descriptors (PCDs) that influence runoff: i) topography, ii) land use, iii) soil type and iv) climate. Factors representing each category were derived for the 30 model and five study catchments from available data. Topographic, land use and soil type factors were derived using ArcGIS.

i) Mean catchment slope and elevation were derived from the DTMs.

ii) Land cover classes used to characterise the catchments examined in Chapter 7 were mapped from year 2000 colour aerial photography for each catchment:

- semi-improved grassland;
- unimproved grassland;
- coniferous plantation;
- broadleaf woodland;
- ericaceous (predominantly *Calluna*) moorland;
- grass/sedge dominated moorland.

iii) Soils present within each catchment were identified by intersecting digital soil data with catchment boundaries, and were subsequently categorised into three broad soil types: blanket peat and raised peat bog, upland soils with peaty topsoils and non-peaty soils (Table 8.2.1), following the descriptions given by Avery (1980). The areal extent of all combinations of land cover and soil type present in each catchment were then derived and converted to percentages (Table 8.2.2).

iv) Long-term mean rainfall (1961-1990) statistics were obtained from the NRFA for the 30 model catchments, and were calculated for each of the five study catchments from rainfall data collated in Chapter 7.

Table 8.2.1. Soils present in catchments selected for runoff modelling, categorised into broad soil type following descriptions by Avery (1980).

Soil type	Blanket peat or raised peat bog	Upland soils with peaty topsoils	Non-peaty soils
Soil sub-groups	*Raw peat soils* 1011a, b; 1013a, b.	Humic rankers 311b, c, d, e; *Stagnopodzols* 651a, b, c,; 652; 654a, b; *Stagnohumic gley soils* 721a, b, c, d, e; *Humic gley soils* 871a.	Brown rankers 313a; *Non-calcareous pelosols* 421a; *Brown earths* 541, c, d, g, j, o, q, r, u, y; 542; 551d; 561a, c; *Argillic brown earths* 572m; *Brown podzolic soils* 611a, b, c; 612b; *Podzols* 631a; *Stagnogley soils* 711, m, n, p; 712a; 713b, d, e, f, g; *Alluvial gley soils* 811a, d, d; 831c; *Sandy gley soil* 861b.

Table 8.2.2. Physical catchment descriptors for model and study catchments (soil and land use variables expressed as percent of catchment). CM: *Calluna* moorland; GM: Grass/sedge moorland; BW: Broadleaf woodland; IG: Improved grass; PL: Plantation; UG: Unimproved grass.

		Catchment characteristics				Soil type			Blanket peat and raised peat bog (BP)				Soils with peaty topsoil (PH)					Non-peaty soil (NP)				
Catchment	Location	Area (km^2)	Slope (degrees)	Ann rainfall (mm)	Altitude (m)	BP	PH	NP	CM	GM	IG	PL	BW	CM	GM	IG	PL	BW	CM	IG	PL	UG
Bedburn Beck	North Pennines	74.5	5.8	894	316	15	46	39	14	0	0	1	0	21	6	1	11	1	9	16	19	1
Brock	North Pennines	34.6	5.7	1360	185	5	28	67	3	2	0	0	8	1	8	49	1	1	0	27	0	0
Burbage Brook	South Pennines	8.4	4.7	1004	385	35	39	26	28	7	0	0	1	13	9	3	0	1	15	0	4	19
Caldew	Cumbria	149.9	7.4	1399	322	14	71	15	3	11	0	0	0	2	13	0	0	1	0	50	4	15
Coal Burn	North Pennines	1.6	2.5	1096	305	88	0	12	0	0	0	88	0	0	0	0	12	0	0	0	0	0
Coquet	North Pennines	60.1	11.1	1020	407	20	56	25	4	15	0	1	0	0	24	0	0	0	2	0	5	48
Croasdale	North Pennines	10.8	8.8	1881	341	39	8	53	36	3	0	0	0	17	24	10	1	0	0	8	0	0
Ding Brook	South Pennines	2.2	7.3	1489	416	58	42	0	0	0	58	0	0	0	0	0	0	0	0	42	0	0
Dunsop	North Pennines	25.1	10.1	1915	364	66	0	34	45	19	0	1	0	5	24	5	1	0	0	0	0	0
East Allen	North Pennines	88.8	5.8	900	385	16	53	30	14	2	0	0	0	13	13	3	1	1	0	48	1	3
East Dart	Dartmoor	22.4	5.2	2088	459	44	15	41	0	44	0	0	0	2	31	2	5	0	1	4	1	9
Eden	North Pennines	67.7	8.3	1483	391	30	38	33	1	29	0	0	0	0	26	6	0	1	3	25	0	9
Esk	Cumbria	70.2	12.7	2305	314	10	39	51	0	10	0	0	0	0	50	0	0	4	0	8	1	26
Gelyn	North Wales	12.8	7.2	2008	423	35	2	63	11	24	0	0	0	5	58	0	0	0	0	0	0	2
Greta	North Pennines	87.0	3.4	1128	403	67	17	16	47	20	0	0	0	7	4	5	0	0	0	16	0	1
Hodge Beck	North York Moors	18.9	8.8	987	323	20	45	36	20	0	0	0	0	26	2	1	6	2	3	26	8	5
Honddu	Brecon Beacons	24.8	14.1	1313	521	15	52	33	4	11	0	0	0	7	26	0	0	0	1	19	2	31
Irfon	Cambrian Mountains	73.2	10.4	1842	412	26	42	32	0	16	0	10	0	0	12	0	20	0	0	14	13	14
Kielder Burn	North Pennines	58.6	7.7	1199	408	56	5	39	17	30	0	9	0	9	7	0	22	0	0	0	1	4
Langdon Beck	North Pennines	12.7	6.7	1462	543	78	8	15	14	63	0	0	0	0	15	0	0	0	0	5	0	3
Lyne	North Pennines	213.2	3.8	1136	170	15	44	41	1	2	3	8	0	0	7	15	18	0	0	43	2	0
Snaizeholme	North Pennines	10.9	10.8	1734	445	17	11	72	0	17	0	0	0	0	63	0	9	0	0	0	2	9
South Tyne	North Pennines	119.3	6.6	1523	513	62	24	14	25	36	0	0	0	0	12	1	1	0	0	11	0	12
Tarset Burn	North Pennines	95.5	4.6	994	300	19	7	73	12	3	0	5	0	8	30	0	35	0	0	3	3	2
Trout Beck	North Pennines	11.6	5.0	1902	656	97	0	3	40	57	0	0	0	0	3	0	0	0	0	0	0	0
Twrch	Cambrian Mountains	20.6	8.6	1533	311	3	63	34	0	1	1	1	0	0	25	7	3	0	0	48	4	11
Usway Burn	North Pennines	22.0	11.2	1056	445	53	29	18	15	12	0	26	0	1	11	0	6	0	0	0	7	22
Warleggan	Bodmin Moor	25.4	5.1	1442	219	11	49	40	0	10	1	0	0	0	30	9	0	6	0	38	0	5
West Allen	North Pennines	79.5	6.6	1155	401	33	32	34	16	18	0	0	0	4	27	3	1	3	0	23	0	6
Ystwyth	Cambrian Mountains	31.5	10.2	1994	455	42	24	34	2	22	0	18	0	1	23	0	10	0	0	2	0	22
Agden	South Pennines	12.2	8.4	1493	355	34	56	8	32	2	0	0	5	18	22	6	3	0	0	5	2	2
Broomhead	South Pennines	21.4	8.5	1493	363	42	14	41	38	4	0	0	4	14	9	7	7	4	14	7	7	9
Langsett	South Pennines	20.9	7.3	1493	394	51	6	40	40	11	1	0	0	17	16	3	4	0	17	3	4	16
Lower Laithe	South Pennines	5	7.8	1385	334	22	17	58	8	14	0	0	0	32	22	3	0	1	0	14	1	1
Keighley Moor	South Pennines	1.5	4.7	1385	405	96	0	0	68	27	0	0	0	0	0	0	0	0	0	0	0	0

8.2.3. Selection of 'model' catchments

The five study catchments examined in Chapter 7 are characterised by a land cover comprising 40-68% *Calluna* moorland (Table 8.2.2). As catchments located in the Cambrian Mountains, Cumbria, Dartmoor and Bodmin Moor contain <5% *Calluna* moorland, catchment hydrology may be significantly different in these regions. For this reason, potential model catchments were firstly limited to those located in the North and South Pennines. This stratification also limits the selection to catchments where climatic factors and soil types are also likely to be more comparable to those within the study catchments.

For Keighley Moor, containing 96% blanket peat, the most comparable catchments identified were Coalburn and Trout Beck containing 88% and 97% blanket peat respectively. Blanket peat catchments can generate rapid runoff (Conway and Millar, 1961) and the water table was found to be within 5 cm of the surface 93% of the time at Trout Beck (Evans *et al.*, 1999). Runoff response might therefore be expected to be comparable within these three catchments. However, Coalburn is an entirely forested catchment while the other two contain no forest cover. As artificial drainage created for forestry management may alter the catchment hydrology, runoff for Keighley Moor was modelled solely on the response at Trout Beck.

The remaining four study catchments Agden, Broomhead, Langsett and lower Laithe contain a range of soil types and land cover making it less straightforward to select comparable catchments. Several criteria were set to exclude potentially different catchments:

- slope – slope in the four study catchments ranges from 7.3-8.5 degrees. As runoff volume increases with slope (Haggard *et al.*, 2005), catchments with slopes >10.0 degrees were excluded;
- soil type – the amount of blanket peat within the four study catchments ranges from 22-51%. Owing to the hydrological behaviour of blanket peat catchments as discussed above, those catchments containing <5% and >85% blanket peat were excluded;
- land use:
    i. none of the study catchments contained any area of plantation on blanket peat, and between 1-20% on other soil types. As artificial drainage created for forestry management may alter catchment hydrology, catchments containing >5% plantation on blanket peat and >30% of the catchment were excluded;
    ii. the study catchments contain 40-68% cover of *Calluna* moorland. Catchments containing <5% *Calluna* moorland were excluded.

This selection process identified seven 'model' catchments (Burbage Brook, Croasdale, East Allen, Greta, Langdon Beck, South Tyne and West Allen). Runoff for Agden, Broomhead, Langsett and lower Laithe was modelled on the average response of these seven model catchments.

8.2.4. Modelling study catchment runoff

For each of the eight model catchments identified above, a runoff:rainfall ratio was calculated for each individual month in available years and then all same month ratios were averaged to determine a mean monthly 'runoff ratio' (i.e. 12 per catchment). Annual mean runoff ratios were also derived for each catchment. For Keighley Moor, mean monthly runoff ratios were taken as those determined for Trout Beck. For Agden, Broomhead, Langsett and lower Laithe, mean monthly ratios were taken as the mean of those determined for Burbage Brook, Croasdale, East Allen, Greta, Langdon Beck, South Tyne and West Allen.

8.2.5. DOC flux estimation

For each study catchment, monthly runoff volumes were estimated for the period of DOC concentration data availability. Rainfall volumes were calculated from monthly rainfall amounts determined in Chapter 7.2.3, multiplied by catchment area. Runoff volume was then estimated by multiplying rainfall volume by the mean monthly runoff ratio determined for that catchment. Monthly DOC flux was estimated as the product of monthly mean DOC concentration (determined in Chapter 7.2.2) and monthly runoff volume, following the method in Buckingham *et al*. (2008). Annual (calendar year) DOC flux was estimated from the sum of monthly values, and was then scaled by the amount of blanket peat within each catchment (the primary source of DOC: McDonald *et al*., 1991) to derive carbon loss per square metre. Trends in DOC flux were identified using the Seasonal Kendall Test (Hirsch *et al*., 1982). Owing to uncertainty in the reliability of early 1980s data (see Chapter 3.5.2), trend analysis was performed over two time periods 1975-2005 and 1990-2005. DOC flux is reported as tC yr^{-1} and tC km^{-2} yr^{-1}. However, it should be noted that the tC km^{-2} yr^{-1} unit is equivalent to gC m^{-2} yr^{-1} commonly used by other authors and referred to later (Section 8.4)

8.2.6. Composition of DOC derived from water colour

DOC concentrations for the five catchments examined in this Chapter were estimated from water colour using the relationship derived in Chapter 6.3.1. The strong linear relationship identified between Hazen and DOC (r^2=0.93, p<0.001, n=181) suggests that humic substances comprise the dominant form of DOC measured for the 50 upland peat catchments sampled in Chapter 5. The specific UV absorbance (SUVA) index can provide an indication of the molecular weight (MW) of natural organic matter (NOM) in water (Edzwald and Tobiason, 1999), thereby allowing inference of the chemical character. Aromatic groups tend to produce a higher SUVA index (Table 8.2.3) and derive from the decomposition of more resistant plant material such as lignin (Killops and Killops, 1993). SUVA is therefore of particular relevance to DOC flux assessment as the index provides additional indication of the origin or age of DOC measured in drainage waters.

SUVA is defined as UV absorbance measured at 254 nm (au m^{-1}) divided by DOC concentration (mg l^{-1}). DOC concentration and water colour (as UV absorbance at a wavelength of 254 nm) were measured for all water samples collected in Chapter 5, and SUVA index calculated for each sample.

Table 8.2.3. Guidelines for the nature of NOM (Edzwald and Tobiason, 1999).

SUVA	Composition
>4	Mostly aquatic humics. High hydrophobicity. High MW.
2-4	Mixture of aquatic humics and other NOM. Mixture of hydrophobic and hydrophilic NOM. Mixture of MWs.
<2	Mostly non-humics. Low hydrophobicity. Low MW.

8.3. Results

8.3.1. Study catchment runoff

Across the 30 potential model catchments, estimated annual runoff ratios ranged from 0.54 to 0.94 (Figure 8.3.1). The range of annual runoff ratios for the catchments selected to model runoff in the study catchments Agden, Broomhead, Langsett and Lower Laithe was smaller (0.62-0.76) suggesting that selection parameters identified catchments with more comparable runoff behaviour. Seasonal variation is evident in the monthly runoff ratios determined for each of the eight model catchments selected (Figures 8.3.2 & 8.3.3), with a higher proportion of rain leaving as runoff between January and March, and lowest between June and August.

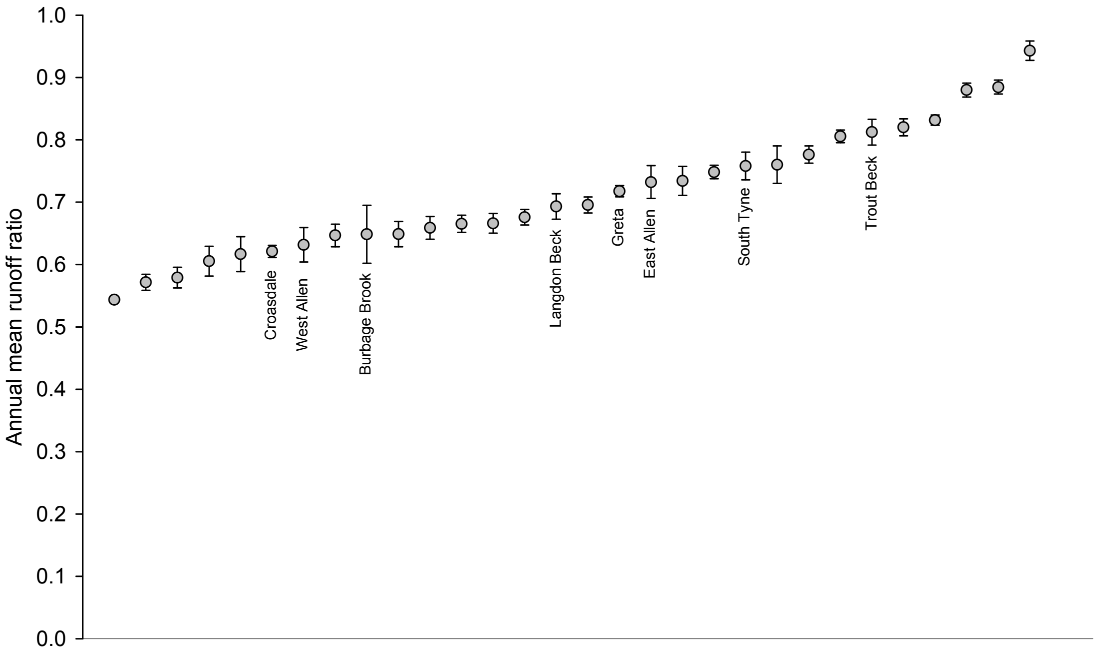

Figure 8.3.1. Range of annual (hydrological year) mean runoff ratios determined for 30 upland peat catchments (error bars show standard error).

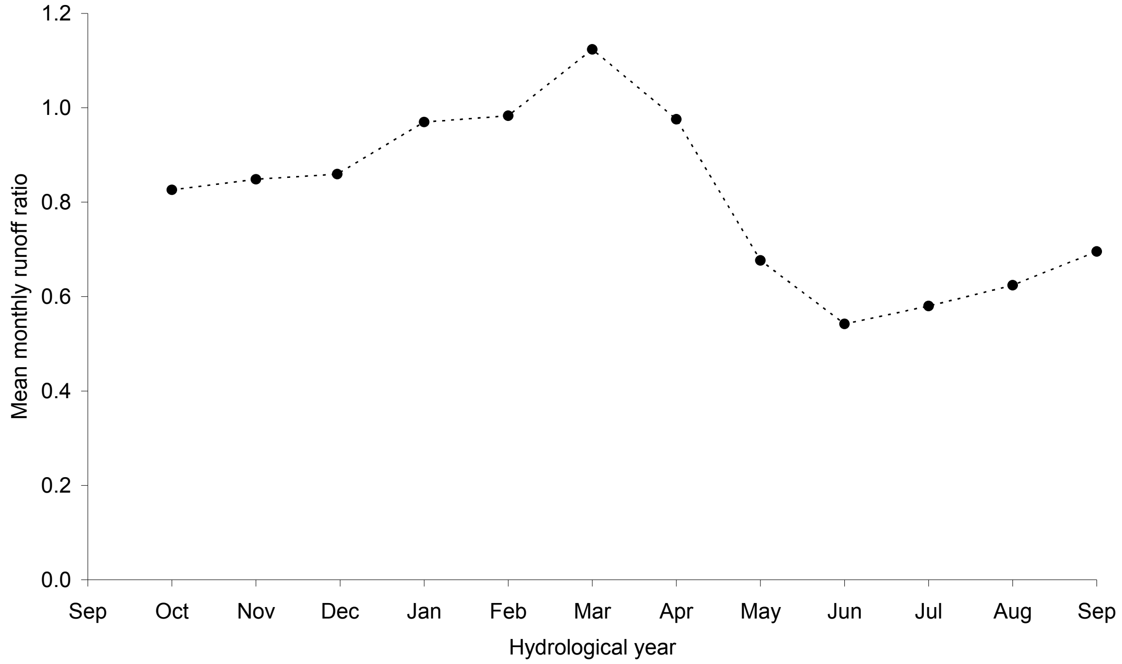

Figure 8.3.2. Mean monthly runoff ratios for Trout Beck catchment, identified to model runoff for Keighley Moor.

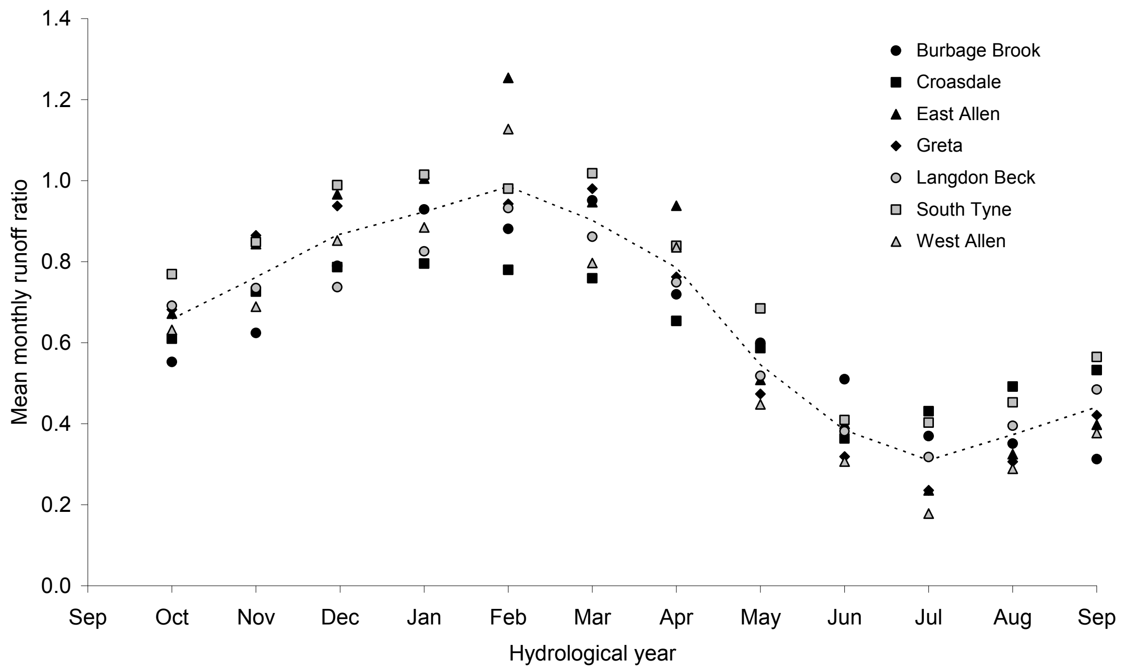

Figure 8.3.3. Mean monthly runoff ratios for seven upland peat catchments identified to model runoff for Agden, Broomhed, Langsett and Lower Laithe catchments (dotted line indicates average values used to model runoff).

8.3.2. DOC flux estimations

1990-2005

For each of the study catchments, the trend in estimated DOC flux showed overall concordance with trend in DOC concentration as might be expected (Figures 8.3.4–8.3.8). However, in years where rainfall was above (1994, 2000) and below average (1996, 2003), DOC flux estimations appear high and low respectively. With the exception of Lower Laithe catchment, highly significant (p<0.001) increasing trends in flux were identified ranging from 0.48-4.67 tC yr^{-1} (0.33-0.48 tC km^{-2} yr^{-1}; Table 8.3.1). Maximum rates of carbon loss in the form of hDOC ranged from 10.3-34.4 tC km^{-2} yr^{-1} (units equivalent to g m^{-2} yr^{-1}).

1975-2005

Over the longer-term, DOC flux estimations for the period 1980-1986 appear consistently high in comparison to the trend in DOC concentration (Figures 8.3.4–8.3.6). Highly significant increasing trends in DOC flux (p<0.001) were still identified ranging from 0.50-1.64 tC yr^{-1} (0.12-0.18 tC km^{-2} yr^{-1}). Estimated rates of carbon loss as hDOC for the three catchments examined here ranged from 8.0-11.8 tC km^{-2} yr^{-1} in 1975/6 to 24.8-29.5 g m^{-2} yr^{-1} in the year 2000.

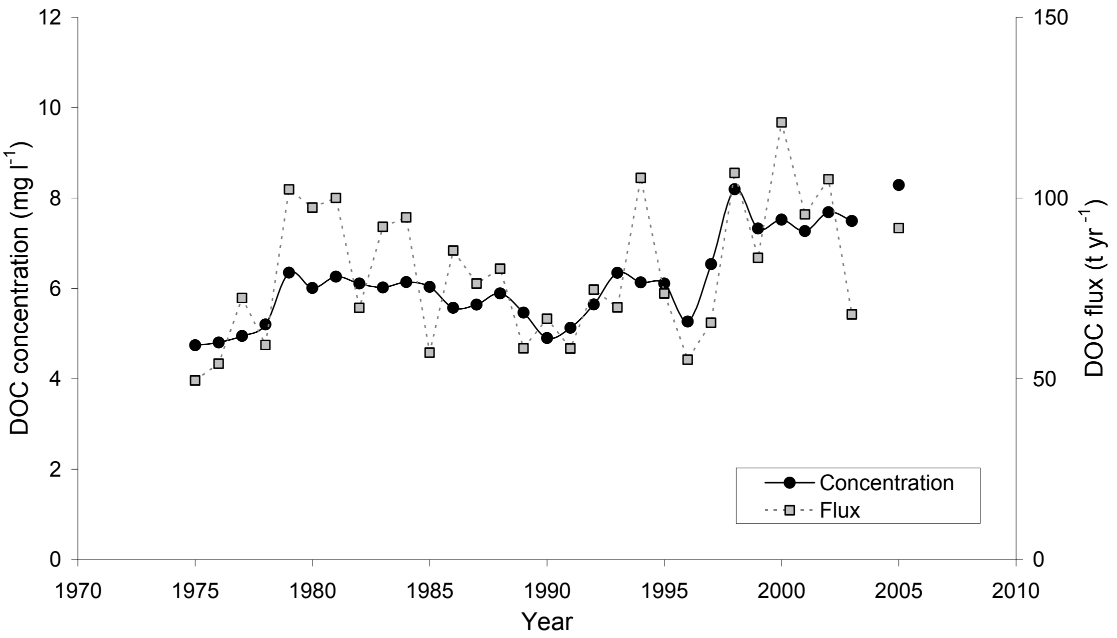

Figure 8.3.4. Annual mean DOC concentration and modelled DOC flux for Agden catchment.

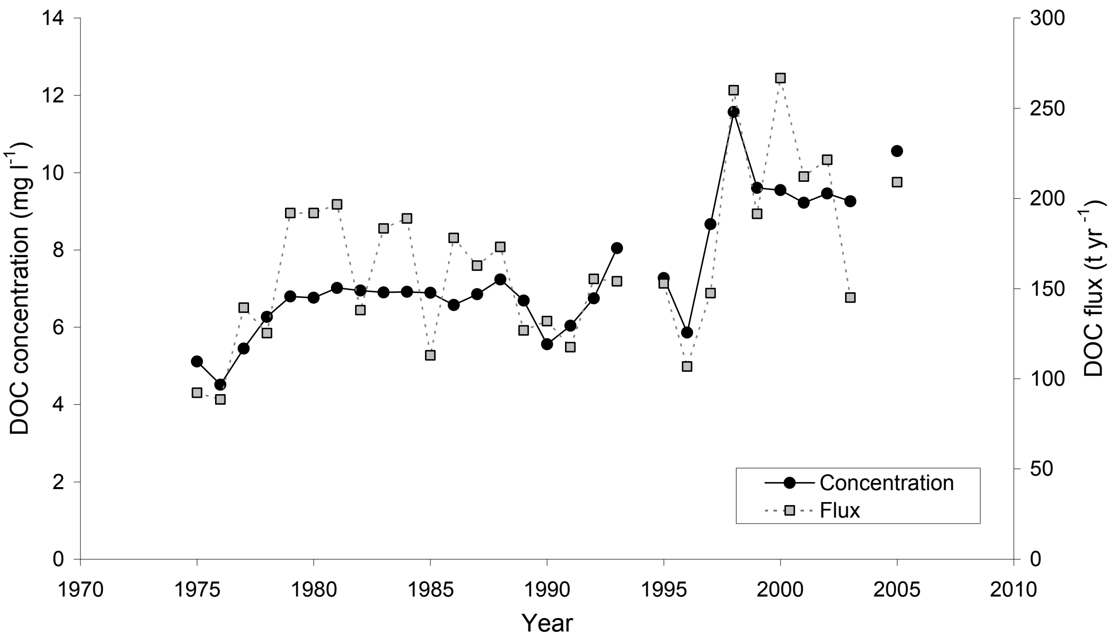

Figure 8.3.5. Annual mean DOC concentration and modelled DOC flux for Broomhead catchment.

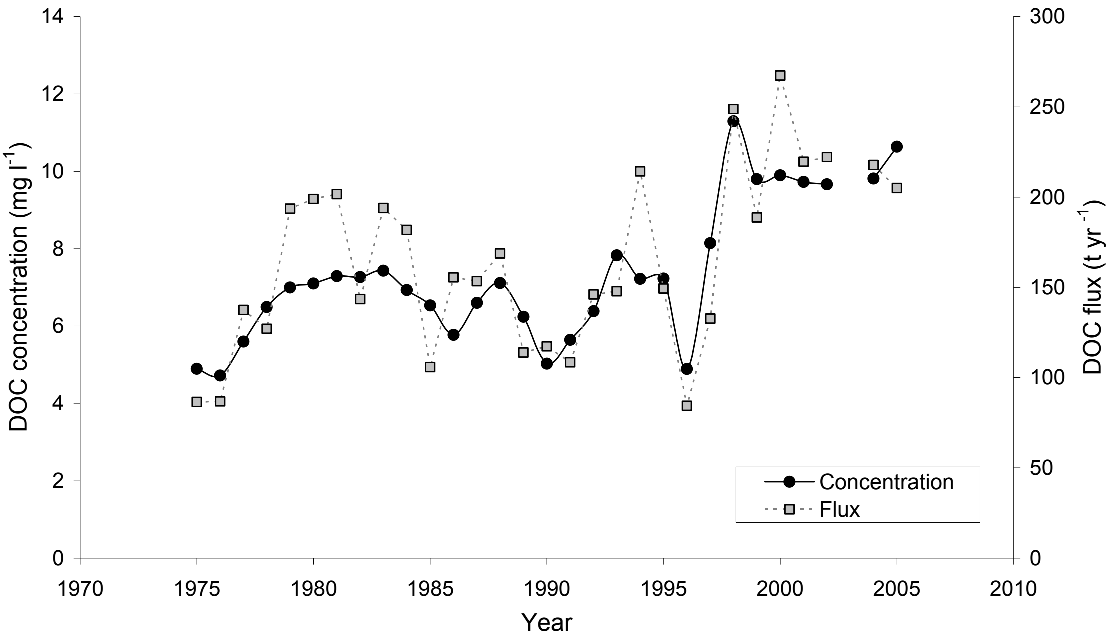

Figure 8.3.6. Annual mean DOC concentration and modelled DOC flux for Langsett catchment.

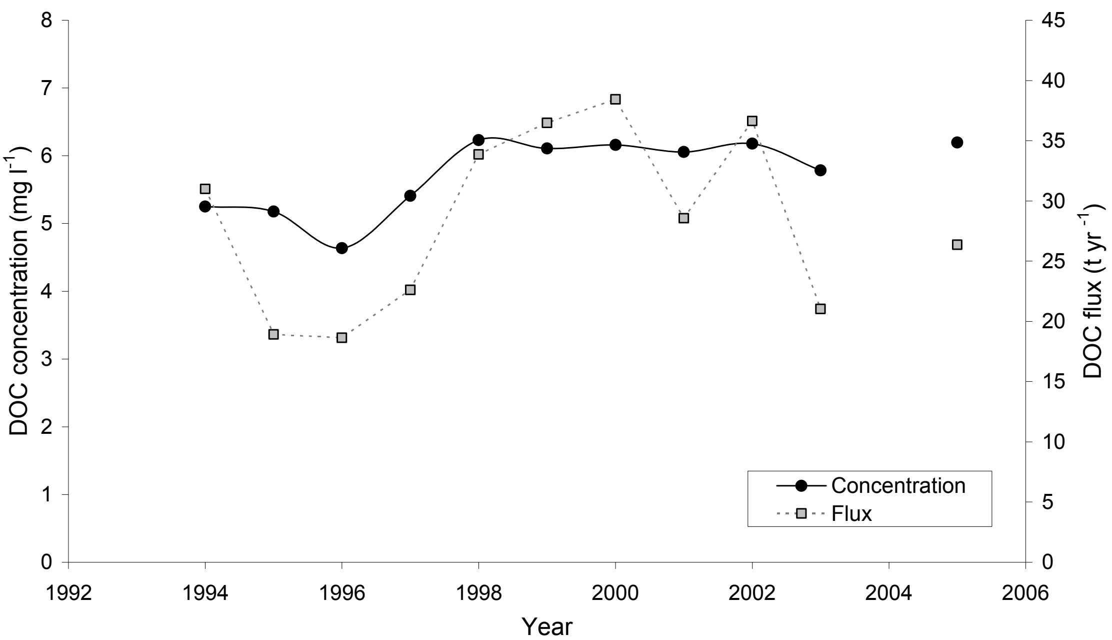

Figure 8.3.7. Annual mean DOC concentration and modelled DOC flux for Lower Laithe catchment.

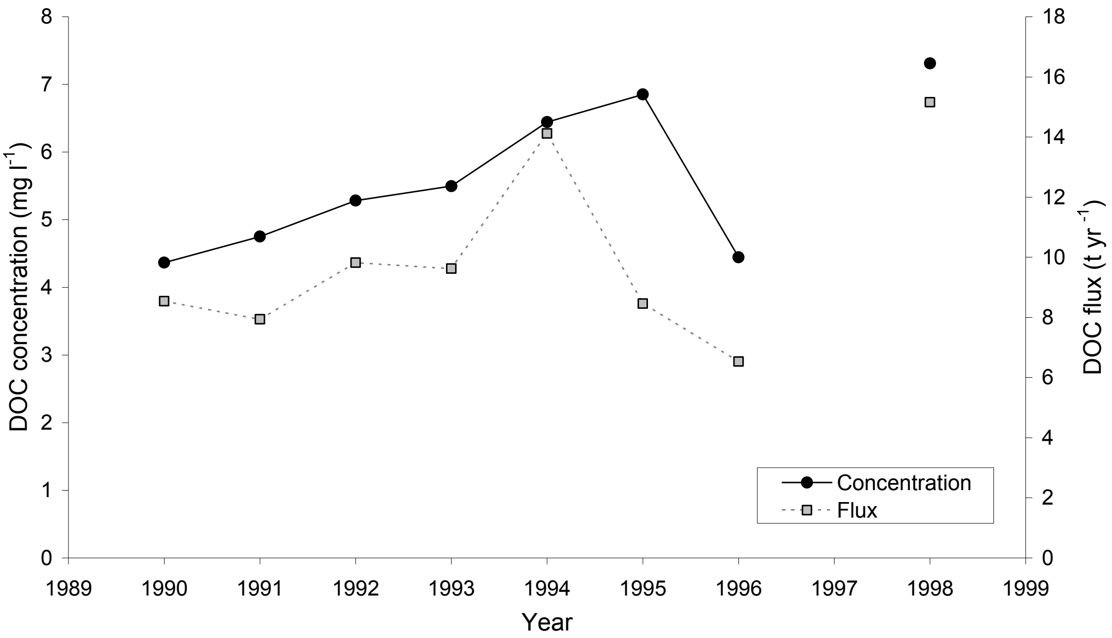

Figure 8.3.8. Annual mean DOC concentration and modelled DOC flux for Keighley Moor catchment.

Table 8.3.1. Trends in DOC flux identified by Seasonal Kendall Test and estimated rates of C loss from blanket peat by study catchment.

Catchment	Area (km^2)	Blanket peat (%)	Trend in DOC flux * 1975-2005 ($tC\ yr^{-1}$)	($tC\ km^{-2}\ yr^{-1}$)	Trend in DOC flux 1990-2005 ($tC\ yr^{-1}$)	($tC\ km^{-2}\ yr^{-1}$)	Range of C loss † ($tC\ km^{-2}\ yr^{-1}$)
Agden	12.2	34	+ 0.50 ***	+ 0.12	+ 1.54 ***	+ 0.37	11.8 – 28.9
Broomhead	21.4	42	+ 1.64 ***	+ 0.18	+ 4.35 ***	+ 0.48	9.8 – 29.5
Langsett	20.9	51	+ 1.49 ***	+ 0.14	+ 4.67 ***	+ 0.43	8.0 – 24.8
Lower Laithe	5.0	22			n.s.	n.s.	16.7 – 34.4
Keighley Moor	1.5	96			+ 0.48 ***	+ 0.33	5.4 – 10.3

* $tC\ km^{-2}\ yr^{-1}$ equivalent to $gC\ m^{-2}\ yr^{-1}$
† estimates for Keighley Moor determined for 1990-1998; *** $p<0.001$; n.s. not significant.

8.3.3. SUVA index

The SUVA index determined for all 181 water samples collected from upland peat catchments was consistently above a value of 2.0 (Table 8.3.2) and correlates with the percent cover of blanket peat within catchments (Figures 8.3.9-8.3.12). The guidelines given by Edzwald and Tobiason (1999; Table 8.2.3), indicate that none of the water sampled in this research contained DOC of purely non-humic origin, and this suggests that both the organic colour and DOC in drainage for the 50 upland catchments sampled derives primarily from the decomposition of blanket and thin peats.

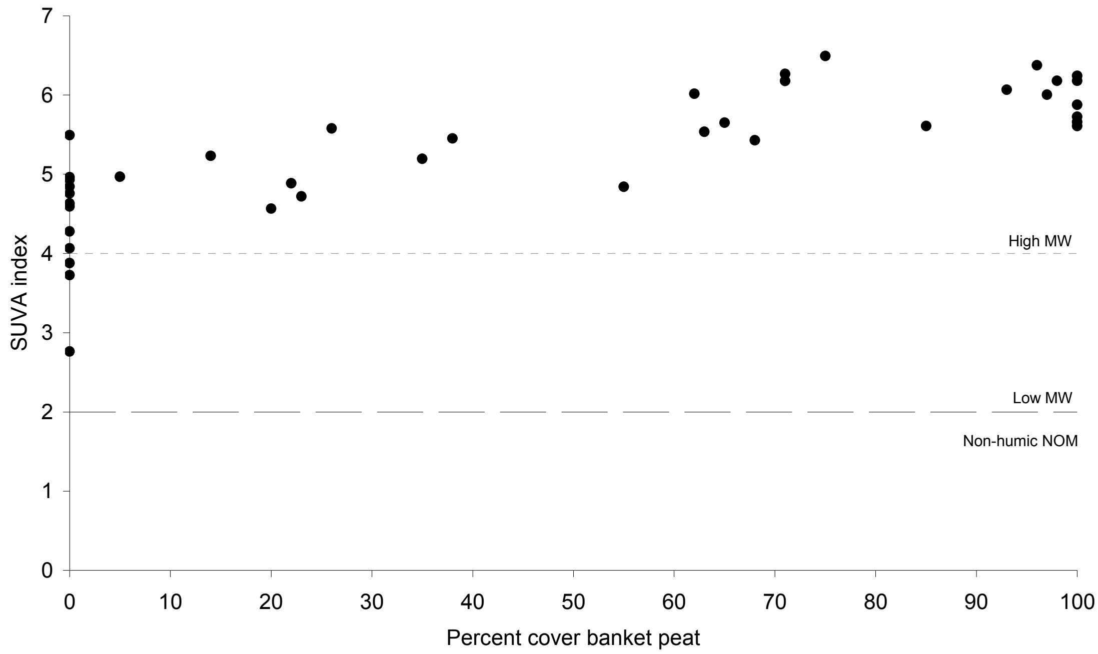

Figure 8.3.9. Percent cover of blanket peat against SUVA in drainage water for 39 catchments sampled in January 2005.

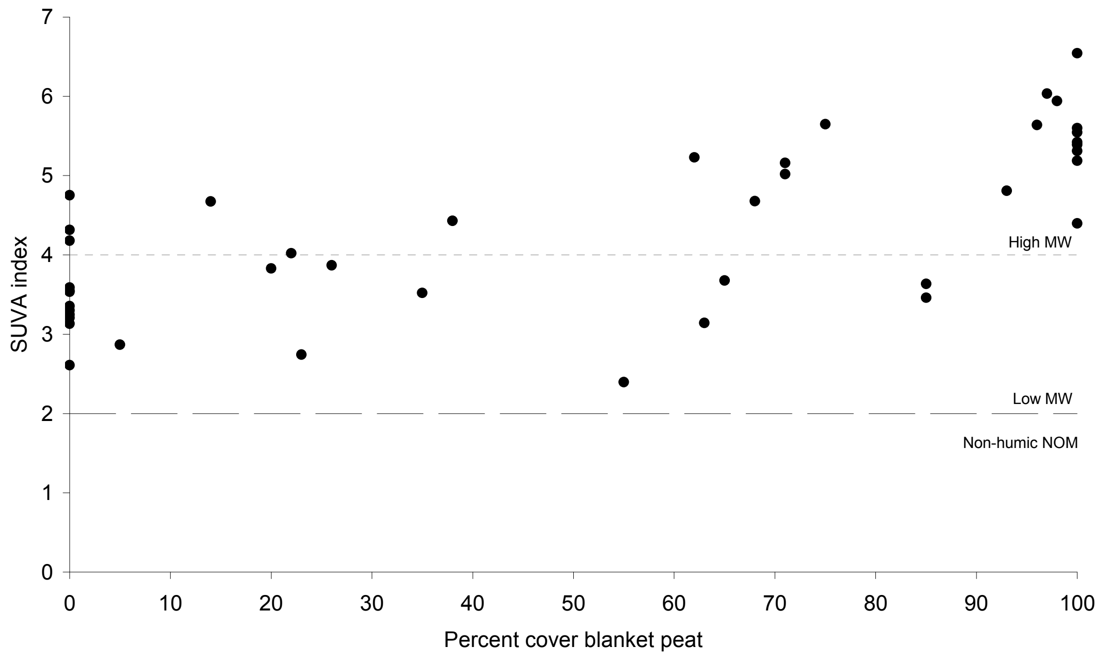

Figure 8.3.10. Percent cover of blanket peat against SUVA in drainage water for 42 catchments sampled in March 2005.

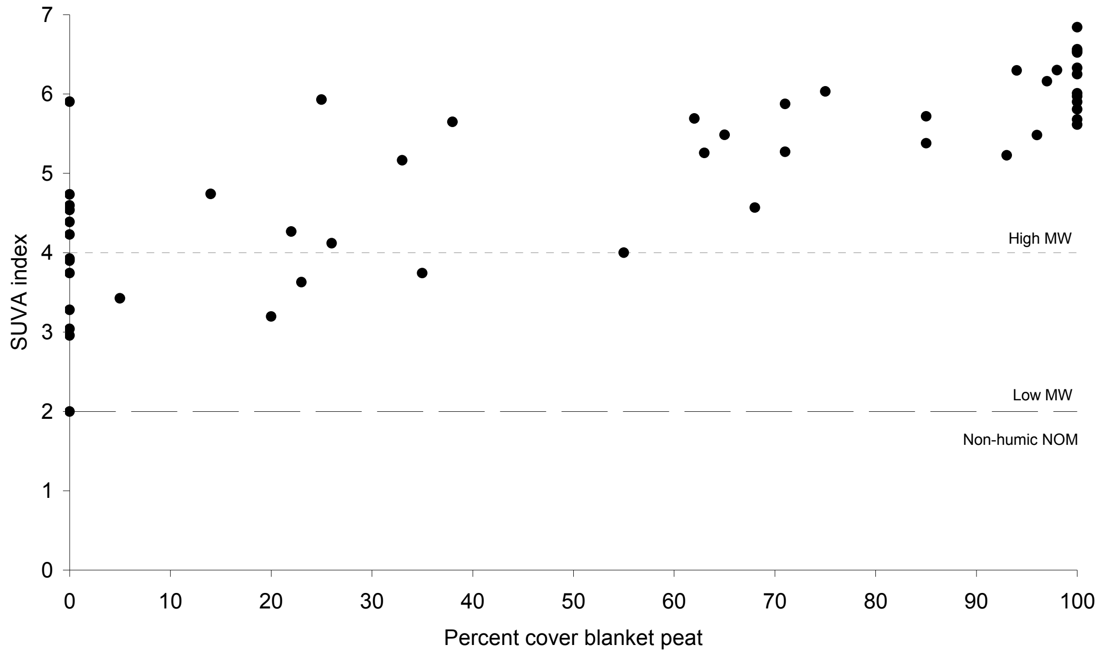

Figure 8.3.11. Percent cover of blanket peat against SUVA in drainage water for 50 catchments sampled in November 2005.

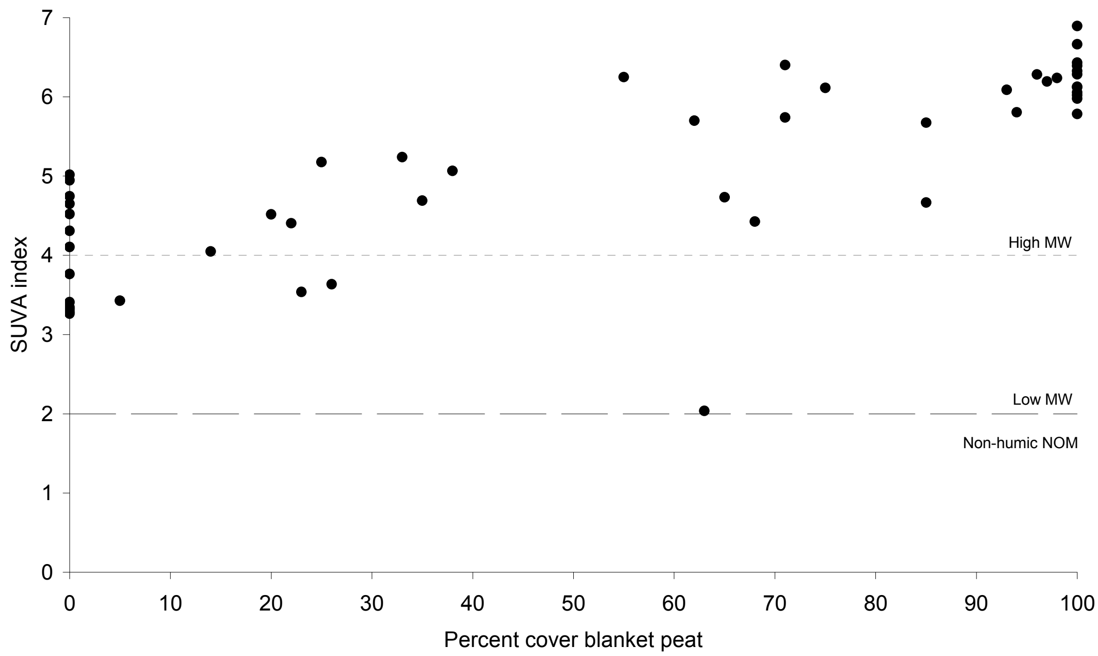

Figure 8.3.12. Percent cover of blanket peat against SUVA in drainage water for 50 catchments sampled in December 2005.

Table 8.3.2. Percent cover of soil type and SUVA in drainage water for 50 catchments sampled in 2005.

	Soil type			SUVA			
Study area	BP	PH	NP	Jan	Mar	Nov	Dec
SY	75	25	0	6.5	5.6	6.0	6.1
SY	20	58	22	4.6	3.8	3.2	4.5
SY	98	2	0	6.2	5.9	6.3	6.2
SY	97	3	0	6.0	6.0	6.2	6.2
SY	94	6	0			6.3	5.8
SY	100	0	0			5.9	5.8
SY	100	0	0	6.2	6.5	6.5	6.4
SY	100	0	0			6.6	6.1
SY	100	0	0			6.3	6.4
SY	100	0	0			6.0	6.1
SY	96	4	0	6.4	5.6	5.5	6.3
SY	0	23	77	4.6	3.1	3.7	3.3
SY	68	32	0	5.4	4.7	4.6	4.4
SY	0	100	0	4.3	2.6	4.4	4.1
SY	85	15	0		3.6	5.4	4.7
SY	38	62	0	5.5	4.4	5.6	5.1
SY	93	7	0	6.1	4.8	5.2	6.1
SY	23	77	0	4.7	2.7	3.6	3.5
SY	71	29	0	6.3	5.2	5.3	6.4
SY	14	86	0	5.2	4.7	4.7	4.0
SY	55	45	0	4.8	2.4	4.0	6.3
WY	100	0	0		5.4	5.8	6.9
WY	100	0	0		5.4	6.0	6.3
WY	100	0	0	5.7	5.5	5.6	6.0
WY	100	0	0	5.7	5.6	5.7	6.0
WY	100	0	0	5.6	5.2	6.3	6.7
WY	63	37	0	5.5	3.1	5.3	2.0
WY	22	78	0	4.9	4.0	4.3	4.4
WY	85	15	0	5.6	3.5	5.7	5.7
WY	35	65	0	5.2	3.5	3.7	4.7
NY	0	87	13	5.5	4.3	4.6	3.3
NY	0	100	0			3.0	5.0
NY	26	74	0	5.6	3.9	4.1	3.6
NY	25	75	0			5.9	5.2
NY	05	91	4	5.0	2.9	3.4	3.4
NY	33	67	0			5.2	5.2
NY	0	100	0	3.9	3.6	3.0	3.3
NY	100	0	0	6.2	5.3	6.5	6.3
NY	0	78	22	4.9	3.2	4.2	4.9
NY	62	37	0	6.0	5.2	5.7	5.7
NY	0	37	63	4.8	3.4	3.9	3.3
NY	100	0	0	5.9	4.4	6.8	6.1
NY	0	100	0	4.8	4.2	4.5	4.7
NY	65	35	0	5.7	3.7	5.5	4.7
NY	71	29	0	6.2	5.0	5.9	5.7
NYM	0	100	0	2.8	4.8	2.0	4.5
NYM	0	100	0	5.0	3.2	5.9	3.8
NYM	0	99	0	4.1	3.3	3.9	4.3
NYM	0	92	8	4.6	3.6	4.7	4.7
NYM	0	95	5	3.7	3.5	3.3	3.4

8.4. Discussion

In the absence of stream-flow data, a data modelling approach was adopted to produce runoff data for the study catchments. The design of the model implemented here predicts runoff as a function of monthly rainfall and therefore allows for the significant seasonal variation observed in runoff generation. For example, in all eight ‘model’ catchments, the highest proportion of rain leaving as runoff is between January and March (Figures 8.3.2-8.3.3). Validation of runoff volumes and hDOC flux estimated for the study catchments using this modelling approach requires measured flow data, and therefore was not possible. However, some assessment of the approach can be made. The range of annual runoff ratios determined for the 30 upland peat catchments selected as potential ‘model’ catchments (0.54-0.94) is comparable to mean annual runoff ratios for upland peat catchments determined in four areas of Scotland (0.44–0.82; Dawson *et al*., 2008). Furthermore, for Agden, Broomhead, Langsett and Lower Laithe catchments, the selection criteria identified seven catchments with a smaller range of annual runoff ratios (0.62-0.76), and comparable trend in seasonal variation (Figure 8.3.3). It must be accepted, however, that the model design does not account for variations in runoff that could be influenced by antecedent soil moisture conditions. Following prolonged dry periods, rates of water table recovery in blanket peats have been shown to be depressed (Evans *et al*., 1999), and in these years mean monthly runoff ratios may over-estimate runoff.

In addition to the relationship found between water colour (Hazen) and DOC in Chapter 6.3.1, the SUVA index determined here for waters sampled from all 50 peat catchments examined in Chapter 5 indicates that no water contained DOC of purely non-humic origin. These observations indicate that both the organic colour and DOC in drainage for the 50 upland catchments sampled derive primarily from the decomposition of blanket and thin peats. This implies that the use of WTW colour data as a surrogate for DOC concentration which represents loss of ‘old’ carbon from decomposition of peat is appropriate.

DOC supply to drainage water is influenced by changes in precipitation and runoff (e.g. Grieve, 1990; Tranvik and Jansson, 2002). There is therefore an inherent degree of circularity in using rainfall and DOC concentration to determine DOC flux. This may explain why the model appears sensitive to above- and below-average rainfall as evident in hDOC flux estimates for all catchments for the period 1990-2005. Lower rates of DOC flux have been determined during drought conditions in other studies (e.g. Scott *et al*., 1998), and this could be indicative of decreased microbial activity (McDonald *et al*., 1991), preferential mineralisation of organic matter releasing carbon as CO_2 (Scott *et al*., 1998), induced hydrophobic properties of humic acids (Hayes, 1987) and peat (Mitchell and McDonald, 1992) or suppression of DOC mobility due to release of SO_4^{2-} from sulphur stored in peat (Clark *et al*., 2005). Above-average rainfall for the period 1980-1986 could maintain higher water tables and provide enhanced flushing of the upper layers of peat (Schiff *et al*., 1998), explaining the consistently high flux estimations for the three catchments examined. However, there was uncertainty about reconstruction of DOC concentrations for this time period (Chapter 3.5.1). Without measured stream flow data, hDOC flux estimations from these catchments cannot be validated, therefore it is not possible to identify the true cause of the deviation of hDOC flux from the general trend of DOC concentration estimated here.

Due to simplifications and potential errors within the model and the data used to derive some periods of the hDOC concentration reconstruction, the estimations of hDOC flux should of course be interpreted with caution. However, estimates of areal carbon loss as DOC from blanket peat in the five South Pennine catchments examined here (5.4-34.4 gC m^{-2} yr^{-1}) are consistent with DOC exports determined from areas of peat or peat dominated catchments in other studies, and these are summarised in Table 8.4.1. Estimates of areal carbon loss from blanket peat in Agden, Broomhead and Langsett catchments for the 1970s (8.0-11.8 gC m^{-2} yr^{-1}) fit entirely within the range of other estimates in the UK. For the period 1990-2005 these losses almost trebled (24.8-29.5 gC m^{-2} yr^{-1}) and are now consistent with higher estimates from upland peat catchments in Scotland (26.2 gC m^{-2} yr^{-1}) and the North Pennines (23.7 gC m^{-2} yr^{-1}). The range of flux estimated for Lower Laithe (16.7-34.4 gC m^{-2} yr^{-1}) appears anomalously high in comparison to the other catchments and could be due an over-estimation of runoff production, but without measured stream flow data this cannot be addressed. However, no significant trend in DOC flux was identified in the data for Lower Laithe and it may be reasonable to assume that this is a valid result. Over-estimation of runoff production could increase the estimates of DOC flux, but between year variations are less likely to differ as rainfall volume appears more significant than runoff in estimating DOC flux using the model implemented here. It is worthy of note that the highest fluxes estimated in the UK in other studies (Table 8.4.1) were determined for Scottish upland peat catchments that are managed for red grouse (Dawson *et al.*, 2002) and rivers draining areas of the north Pennine AONB (Worrall *et al*., 2008), where over 20% of the area shows evidence of recent burning (Yallop *et al*., 2006b). Several of the catchments examined by O'Brien *et al*. (2008) are also managed for red grouse, but DOC flux estimations appear significantly lower. This may arise from the period of study being later than year 2000 where the highest flux was determined in this study. For the period 2002-2005 DOC flux estimations for Agden, Broomhead and Langsett are more consistent (16.0-25.2 gC m^{-2} yr^{-1}).

Table 8.4.1. Carbon flux studies from peat and peat-dominated catchments.

Study catchment (peat coverage %)	C-flux (g m^{-2} yr^{-1})	Study period	Reference
Scotland			
Scottish highlands (peat-dominated)	7.0 – 10.3	1993	Hope *et al*. (1997b)
Brocky Burn upper (67)	17.4 – 21.4	1996-1998	Dawson *et al*. (2008)
Water of Charr (81)	16.9 – 26.2	1996-1998	Dawson *et al*. (2008)
England			
Rivers Tees and Coquet, North Pennines	3.6 – 23.7	1970-2005	Worrall *et al*. (2008)
South Pennines 1970s (100)	**8.0 – 11.8**	**1975-1976**	**This study**
Great Dunn Fell, North Pennines (c.50)	7 – 15	1992-1996	Scott *et al*. (1998)
Moor House, North Pennines (97)	9.4 – 15	1999	Worrall *et al*. (2003a)
Upper North Grain, Peak District (100)	15.4	2005-2006	Pawson *et al*. (2008)
Dark Peak, Peak District (100)	5 – 18	2002-2006	O'Brien *et al*. (2008)
South Pennines 2000s (100)	**16.0 – 29.5 (highest)**	**2000-2005**	**This study**
Wales			
Upper Hafren, Mid-Wales (peat dominated)	8.4	1996 - 1998	Dawson *et al*. (2002)
Northern Europe			
Salmisuro mire complex, Finland (79)	4.2 – 11.3	2006 - 2007	Jager *et al*. (2009)
USA			
Peatlands, Minnesota (100)	8.9 – 27.6 (lowland bog)	1981 - 1985	Urban *et al*. (1989)
Canada			
Mer Bleue Bog, Ontario (100)	8.3	1998 - 1999	Fraser *et al*. (2001)
Bois-des-Bel peatland, Quebec (100)	3.5 – 4.8 (restored) 6.2 – 10.3 (cutover)	1999 - 2001	Waddington *et al*. (2008)

Unfortunately data that could be used to derive carbon flux estimates for other fluvial and gaseous components of carbon budgets for the five study catchments are not available. Carbon budget calculations for an upland blanket peat catchment in the North Pennines (Worrall *et al*., 2003a; Table 8.4.2) may provide the most comparative data. Substitution of the export of carbon loss as DOC estimated for Moor House catchment with the range of exports as DOC estimated for Agden, Broomhead and Langsett catchments in the South Pennines would suggest that these catchments would move from being net carbon sinks in the 1970s to net sources post year 2000.

Table 8.4.2. Summary of carbon exports and inputs for the Moor House catchment (from Worrall *et al*., 2003a).

Input/output route	Areal input/export rate (gC m^{-2} yr^{-1})	Range (gC m^{-2} yr^{-1})
Rainfall DIC	1.1	
Rainfall DOC	3.1	
CO2	55.0	40 to 70
CH4	-7.1	-1.5 to -11.3
DOC	-9.4	-9.4 to -15
POC	-19.9	-2.7 to -31.7
Dissolved CO2	-3.8	-2.0 to -3.8
DIC	-5.9	-4.1 to -5.9
Weathering DIC	1.8	0 to 1.8
Total	14.9	13.8±15.6

Positive values represent an input to catchment.

The identification of increasing trends in DOC flux in the four study catchments where increases in the area of controlled burning were identified as being strongly and positively related to increasing DOC concentrations (Chapter 7) provides further evidence of a causal mechanism between the area of vegetation burn and enhanced decomposition of blanket peat. That increases in DOC flux were identified also indicates that increasing DOC concentrations are not merely related to changes in rainfall and discharge in the studied catchments, as has been observed elsewhere (Worrall *et al*., 2003b). This observation is of particular relevance in the context of current research focussed on carbon dynamics in peatland ecosystems, as DOC concentration records are often the only carbon data available 'off the shelf'. While DOC flux quantifies the 'amount' of carbon indicated by DOC concentration, this study provides further evidence that DOC concentrations may also provide good estimation of loss of carbon from peat via fluvial pathways.

The results of DOC flux modelling presented here suggest that some blanket peats in South Pennine catchments, currently managed as grouse moors, may be losing carbon in the form of DOC at rates of up to 24-29 gC m^{-2} yr^{-1}. Significant relationships were identified between the area of vegetation burn on blanket peat and DOC concentration for the period 1976-2005 (Chapter 7.3.3). Although potential errors in derivation of DOC flux for the study catchments have been discussed, the effect of controlled burning on carbon loss from blanket peat was speculatively estimated for the area of blanket peat located within Agden, Langsett and Broomhead catchments (24 km^2). Regression of total area of Class 1 burn against areal loss of carbon as DOC from this area of blanket peat for the period 1976-2005 indicates that background DOC efflux from blanket peat in the South Pennines (i.e. with no controlled burning) to be 8.88±2.5 t km^{-2} yr^{-1} and that each 1 km^2 of new burn effects an increase in areal loss of carbon of 2.85±0.81 t km^{-2} yr^{-1} (Figure 8.4.1). As each Class 1 burn scar is visible in aerial imagery for just over four years (Chapter 4.3.4) each 1 km^2 of burn could effect an increase in loss of carbon of up to 11.48 tC. Controlled burning, implemented at the intensity determined here (20%), has at least doubled the carbon loss as DOC from blanket peat.

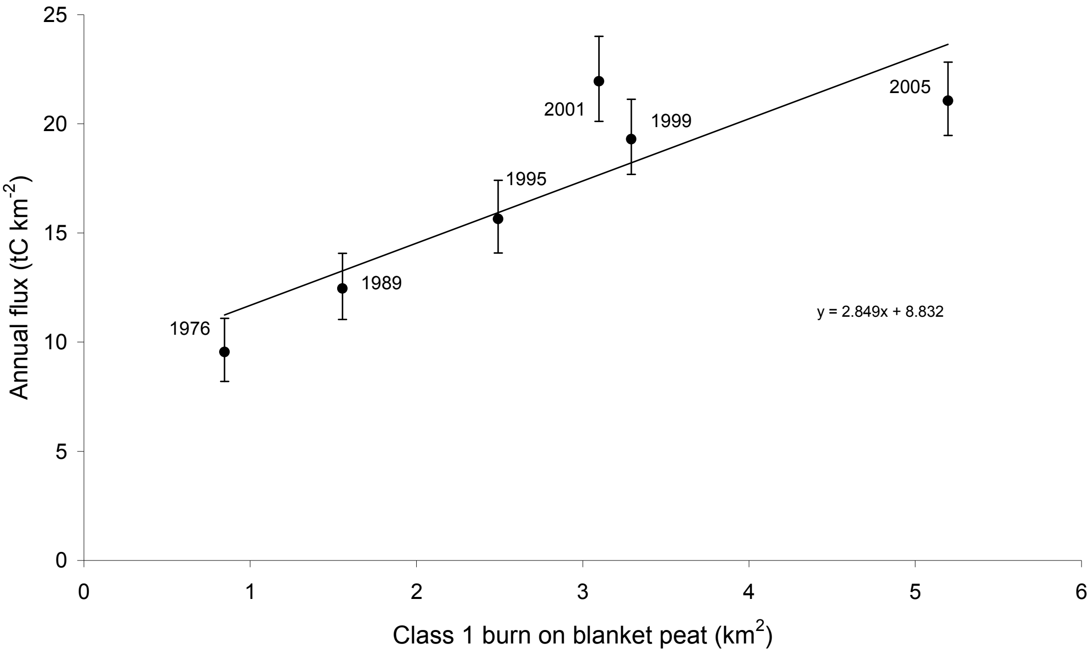

Figure 8.4.1. Area of Class 1 burn on blanket peat against areal loss of carbon from blanket peat in Agden, Broomhead and Langsett catchments (r^2=0.70; *p*=0.024).

8.5. Conclusion

The rainfall-runoff model developed in this chapter predicts mean monthly runoff behaviour in the upland peat catchments examined. Although validation of runoff was not possible, DOC flux estimates are consistent with DOC exports in other studies. DOC flux estimated for five catchments here showed general concordance with trends in DOC concentration, although the model appears sensitive to above- and below-average rainfall.

Estimates of areal carbon loss from blanket peat in Agden, Broomhead and Langsett catchments for the 1970s (8.0-11.8 gC m^{-2} yr^{-1}) are within the lower range of carbon loss estimated for other upland peat catchments in the UK. Estimates for the period 1990-2005 (24.8-29.5 gC m^{-2} yr^{-1}) are now consistent with higher estimates from upland peat catchments in Scotland (up to 26.2 g m^{-2} yr^{-1}) and the North Pennines (up to 23.7 g m^{-2} yr^{-1}) where controlled burning is also undertaken. The increases identified in DOC fluxes demonstrate that the increasing DOC concentrations examined in Chapter 7 are not merely related to changes in rainfall and discharge. The data provide further evidence of a causal mechanism between vegetation burning and enhanced decomposition of blanket peat. Each 1 km^2 of burn on blanket peat could effect an increase in carbon loss of up to 11.48 tC.

Chapter 9: Synopsis

Peatlands are unbalanced ecosystems in which the rate of production of organic matter exceeds the rate of decay (Moore and Bellamy, 1974). Over 85% of peat deposits in the UK formed as blanket bogs (Lindsay, 1995) and are predominantly found in upland areas. These peatlands began accumulating between 4000-8000 years BP creating blanket peats up to 6-7 m deep in places (Charman, 2002). Peats typically comprise 65% organic matter (Clymo, 1983) and in the UK account for 50% of total soil carbon (Milne and Brown, 1997).

Carbon loss from peat soils as DOC forms a significant component of peatland carbon budgets (Meybeck, 1993; Pastor *et al*., 2003; Worrall *et al*., 2003b; Billet *et al*., 2004). Increasing trends in DOC concentration have been observed in surface waters globally (e.g. Stoddard *et al*., 2003; Vuorenmaa *et al*., 2006); however, those reported in the UK have been notably larger (Skjelkvåle *et al*., 2005). Increases in DOC flux concomitant with increases in DOC concentrations (Worrall *et al*., 2003b) indicate that increased loss of carbon is occurring. Indeed some UK peatlands are close to (Worrall *et al*., 2003a) or at best (e.g. Billet *et al*., 2004) carbon neutral. Considering the global significance of the carbon pool that peatlands contain (Gorham, 1991), depletion of this store could have significant implication for global warming (e.g. Jenkinson *et al*., 1991).

Regional- and global-scale factors suggested to influence the export of carbon from peat, including severe drought (Worrall and Burt, 2004), climatic change (Freeman *et al*., 2001a) and reductions in acid deposition (Evans *et al*., 2006) do not fully explain smaller-scale spatial variation (Yallop *et al*., 2008) or long-term temporal change (e.g.

Worrall *et al*., 2003b) in DOC concentrations observed in the UK, as demonstrated by Monteith *et al*. (2007). The aim of the research presented in this thesis has been to examine the potential effects of land use and management on spatial and temporal variation in drainage DOC concentration from upland peat catchments in the UK. The evidence presented in this thesis provides greater understanding of the influence of localised factors on DOC production and release from upland peat soils.

9.1. Main findings

Spatial variability in drainage DOC concentration has been noted across the UK (e.g. Dawson *et al*., 2002; Monteith and Evans, 2005) and has been found to relate to stream discharge (Grieve, 1984), and physical catchment characteristics including catchment slope (e.g. Aitkenhead *et al*., 1999), altitude (e.g. Hope *et al*., 1997a) and cover of blanket peat (McDonald *et al*., 1991; Aitkenhead *et al*., 1999; Chapman *et al*., 2001). The data presented in this thesis show that variability in drainage DOC concentration exists between upland peat catchments in the South Pennines and North Yorkshire Moors, and a significant relationship was found to exist between the cover of blanket peat and DOC concentration. However, of the 20 catchment characteristics tested, the proportion of new burn on blanket peat was shown to be the most significant predictor of drainage DOC in three of the four study regions examined in Chapter 5. None of the catchments examined in the fourth region contained any cover of blanket peat. Assessment of rainfall prior to sampling of catchment drainage shows that this effect did not arise as a result of differences in stream discharge.

The effect of burning management on drainage DOC concentration as identified for catchments covering areas of less than 3 km^2 was also important for larger-scale reservoir catchments as shown in Chapter 6. Again the proportion of new burn on blanket peat was found to be the most significant predictor of DOC concentration and demonstrates that burning is a significant driver of landscape-scale variation in DOC. The results are consistent with Yallop *et al*. (2008) who identified a significant relationship between the area of burn on blanket peat and drainage water colour. Furthermore, ten of the catchments examined by Yallop *et al*. (2008) were included in the research here, and that no significant difference was identified between the blanket peat burn-DOC regression models for these ten catchments, and the remaining 40 catchments examined here, demonstrates that the catchments examined previously are not atypical in the South Pennines, but part of a widespread response at least across this area.

Indeed the evidence presented here demonstrates that the dynamics of carbon cycling in blanket peat have been altered over the recent past. The importance of the amount of blanket peat in determining DOC concentrations in surface waters (e.g. Aitkenhead *et al*., 1999), although obviously still a major determinant as can be seen by the significant blanket peat-DOC regression, is no longer the primary factor controlling spatial variability in the areas examined. This is highlighted in the data presented for both small headwater catchments and reservoir catchments. Assessment of 19 catchments (<3 km^2) with blanket peat coverage >85%, effectively removing the influence of extent of blanket peat from analysis, showed that 50% of the variance in DOC concentration can be explained by the area of new burn. Also, for the nine reservoir catchments examined

(1.5-22 km^2), the degree of variance in DOC concentration explained by the cover of blanket peat reduced from 48% in 1999 to 37% in 2005. Most striking, however, from the perspective of considering the increasingly important role of burning as a determinant of increases in DOC over the recent past, is the observation that over this period, for catchments where no increase in the area of burn on blanket peat was identified, increases in DOC were minimal (Figure 6.3.5).

No relationships between burning on other soil types and DOC concentration were identified at either spatial scale examined, indicating that it is not fire use *per se* that affects DOC production, but its application in blanket peat environments. That no significant relationships between any land use or soil type factor and DOC were identified for catchments containing no blanket peat shows that the primary source of DOC in drainage for the catchments examined is the decomposition products from blanket peat. This would indicate that for the examined catchments the increase in DOC results from loss of 'old' carbon (humic DOC: hDOC) rather than changes in decomposition of senescing plant growth. This is supported by the strong linear relationship identified between water colour (Hazen) and DOC concentration in Chapter 6, and the consistently high values of SUVA determined for these catchments in Chapter 8.

In longer-term data for five reservoir catchments in the South Pennines examined in Chapter 7, significant relationships were found to exist between temperature, sulphate deposition and controlled burning factors and hDOC concentration. The annual variability in climate and acid-deposition factors explain the same degree of variance in hDOC concentration for the period 1990-2005 for some, but not all catchments (SO_4^{2-} deposition: r^2=0.21-0.31; temperature: r^2=0.28-0.31). Interestingly, no cumulative effect or interaction between temperature and acid deposition was identified, though it is not clear why this might be. For the period 1990-2005, the data indicate that the 0.75˚C temperature increase determined accounts for a 5-20% rise in hDOC concentration in these catchments, which is consistent with estimates from other studies (Worrall *et al*., 2004; Evans *et al*., 2006). That the driver of a 5-20% change in hDOC concentration is climatic change rather than changes in acid deposition is supported by observations that neither catchment-scale acidification (Lydersen *et al*., 1996) nor acid-exclusion (Wright *et al*., 1993) experiments had significant effect on DOC concentrations. Increasing DOC concentrations have also been observed in other parts of the UK experiencing very little or no anthropogenic sulphate deposition (Evans *et al*., 2005).

The proportion of new burn on blanket peat was identified to be related to drainage hDOC concentration for all five catchments examined, and for the period 1990-2005, explains more than twice the degree of variance in hDOC concentration than the other tested factors (r^2=0.68-0.98). The new burn on blanket peat-hDOC relationship was also significant for the three catchments examined for the longer-term period 1966-2005 (r^2=0.48-0.75). The importance of burn management on hDOC production in blanket peat is highlighted strongly by the data for one catchment, Lower Laithe, where between 1999 and 2005 there was no observed increase in the extent of burning on blanket peat and no significant increase in annual hDOC (Figure 7.3.10). As it is reasonable to assume this catchment, located less than 5 km to the south of Keighley Moor, has experienced the same changes in climate and acid deposition, it clearly highlights the overall low importance of these two proposed explanations of increasing drainage DOC concentrations (Freeman *et al*., 2001; Evans *et al*., 2005, 2006; Monteith *et al*., 2007) for upland catchments in central England.

The data presented in Chapters 6 and 7 provide persuasive evidence that the area of new burn on blanket peat is a highly significant driver of DOC production and in catchments where the area of burn has not changed, increases in DOC production have been minimal. The strong and highly significant, positive relationship between changes in burning and hDOC concentrations over the recent past may also help explain the larger increases in DOC concentration observed in the UK than elsewhere (Skjelkvåle *et al*., 2005), or why other suggested drivers cannot explain the same degree of variance in the UK as in other regions globally as shown by Monteith *et al*. (2007). This research provides valuable evidence of changes in peatland carbon cycling in the UK, and the data suggest that localised land management has a significant influence on carbon dynamics in blanket peats. These data imply that increased degradation of peat is occurring where burning is common and therefore has considerable implication for ecosystem services such as water provision and also for blanket bog habitats. Up to 13% of the global expanse of blanket bog occurs in the UK (Ratcliffe and Thompson, 1988), and over 20% of blanket bog declared as SSSI in the North Pennines AONB show evidence of recent burn activity (Yallop *et al*., 2006b). Concerns regarding the potential negative effects of controlled burning on the degradation of blanket bogs have already been raised (Tucker, 2003; Stewart *et al*., 2004).

The data modelling approach adopted in Chapter 8 has allowed the importance of carbon loss from blanket peats to be quantified. hDOC flux estimated for the five catchments examined in Chapter 7 showed general concordance with trends in hDOC concentration, and demonstrates that the increasing hDOC concentrations represent real increasing loss of carbon from upland peat. This observation is of particular relevance in the context of current research focussed on carbon dynamics in peatland ecosystems, as DOC concentration records are often the only carbon data available 'off the shelf' and allow both widespread and historical reconstructions such as those undertaken here. The study provides further evidence that DOC concentrations may provide good representation of loss of carbon from peat via fluvial pathways.

The blanket peats in Agden, Broomhead and Langsett catchments were estimated to be producing between 8.0-11.8 gC m^{-2} yr^{-1} in the 1970s, on par with lower estimates of carbon loss as DOC from other peat catchments across the UK in the 1990s. It is interesting to note that these estimates changed to between 24.8-29.5 gC m^{-2} yr^{-1} for the period 2000-2005, matching higher estimates of carbon loss from upland peat catchments in Scotland (up to 26.2 gC m^{-2} yr^{-1}: Dawson *et al*., 2004) and the North Pennines (up to 23.7 gC m^{-2} yr^{-1}: Worrall *et al*., 2008) where controlled burning is also undertaken. Increasing DOC fluxes provide further evidence of a causal mechanism between vegetation burning and enhanced decomposition of blanket peat. Each 1 km^2 of burn on blanket peat appears to effect an increase in carbon export as DOC of up to 11.48 tC (11.48 gC m^{-2}). Considering the size of DOC (<0.45 μm) this figure is striking, as carbon losses as POC (all organic material >0.45 μm) from peat catchments in the UK generally range up to 20 gC m^{-2} yr^{-1} (e.g. Worrall *et al*., 2003a), with higher estimated losses from eroding peatlands in the South Pennines of 38.82 gC m^{-2} yr^{-1} (Labadz *et al*., 1991) to 73.97 gC m^{-2} yr^{-1} (Pawson *et al*., 2008).

It is probable that burning also has implications for carbon losses from blanket peat by other pathways especially as gaseous CO_2 from respiration, but this was not assessed in this study. Furthermore, higher proportions of DOC are exported from peat catchments during storm events and could result in underestimation of DOC efflux (Clark *et al*., 2007). However, it is not clear how peak inputs of DOC might be buffered by reservoir cycling (Pattinson *et al*., 1995) and therefore the potential impact on flux estimations determined in this research. In-reservoir (Pattinson *et al*., 1995) and in-stream (Dawson *et al*., 2001) removal of DOC by biological degradation, evasion of CO_2 from stream water (Hope *et al*., 2001) and efflux of POC which is significant from southern Pennine blanket peat (Labadz *et al*., 1991; see above) are further components of peatland carbon cycling that require further assessment to fully understand the implication of controlled burning on national carbon budgets.

9.2. An underlying causal mechanism

The evidence that controlled burning of vegetation on blanket peat enhances DOC production requires an underlying potential causal mechanism, otherwise the data here are merely correlation. Decomposition processes in blanket peat are primarily microbially mediated (e.g. Moore and Bellamy, 1974; Tipping and Hurley, 1988; McDonald *et al*., 1991) suggesting that increases in DOC production result from increased activity of both aerobes (e.g. *Bacillus sp*: Martin *et al*., 1982) and facultative anaerobes (Martin *et al*., 1982), as well as other soil biota (e.g. Cole *et al*., 2002;

Carrera *et al*., 2009). The most parsimonious interpretation of the relationship between area of new burn on blanket peat and DOC production and release is that exposure of the peat surface as a result of fire improves conditions for microbial activity.

Moorland burning is known to modify the vegetation of saturated bogs, specifically the replacement of *Sphagnum*-rich moss communities (the primary producer of blanket peats in the UK: Lindsay, 1995) with drier *Calluna vulgaris* and *Eriophorum vaginatum* heath habitat (Pearsall, 1941; Ratcliffe and Thompson, 1988). Such change in vegetation is highly indicative of induced hydrological change and potentially increased oxygenation of soil profiles that would be anoxic in unaltered bog environments. The mean area of exposed peat surface in new burns surveyed in 2005 was found to be 79%, and the median duration of this burn class is estimated to be just over four years (Chapter 4). Removal of vegetation canopy will result in greater exposure to solar irradiation and this, together with the lower albedo bare peat has compared to vegetated moorland (Pereira, 1973), will result in greater absorption of solar radiation. The importance of this might reasonably be expected to be limited to summer months as this is the period of peak interstitial DOC production (Mitchell and McDonald, 1992; Scott *et al*., 1998) and increases in surface temperatures of up to 5-7˚C on peat exposed by burning relative to that under a complete canopy of bog species has been noted over this period (Fullen, 1983; McDonald *et al*., 1991). Increases in DOC release from peat soils due to enhanced microbial activity as a consequence of higher temperatures have been observed in both laboratory (Freeman *et al*., 2001a) and field conditions (Tipping *et al*., 1999; Clark *et al*., 2005) indicating that this may be one possible driver for elevated levels of DOC release in heavily burned catchments.

Removal of canopy will also expose the peat surface to erosion (Imeson, 1971; Yeloff *et al*., 2006), freeze-thaw processes (Maltby, 1990) and higher wind speeds which could promote higher evaporation (Fullen 1983; McDonald *et al*., 1991). Increased soil porosity (Mallik and Fitzpatrick, 1996), infiltration and throughflow (Imeson, 1971) found in soils following burning, also indicate considerable alteration of the saturated and anaerobic hydrological conditions expected to occur in blanket peat. Drying of the soil profile in these environments where decomposition is primarily restricted by anaerobic and reducing conditions, would be expected to create opportunities for greater aerobic microbial activity. This would result in enhanced peat decomposition and DOC production, as well as loss by CO_2.

Enchytraeid worms are suggested to contribute 26% of DOC production in blanket peats (Cole *et al*., 2002) and have also been shown to enhance microbial activity (Cole *et al*., 2000). Increased numbers of enchytraeids in surface layers of soil following burning (Maillik and Fitzpatrick, 1996) provides a further plausible link between increases in controlled burning and enhanced DOC production. How the intensity of burn management alters the effect of individual burn patches on decomposition processes in blanket peat was not assessed here and remains unclear. Where new burns occur adjacent to or even across recovering burns, as is now evident in many areas of the North Pennines (Yallop *et al*. 200b), there could be a cumulative negative effect on carbon dynamics.

Despite the evidence presented in this thesis, it must noted that a number of previous studies have failed to identify a link between burn management and enhanced DOC production. Ward *et al*. (2007) found no difference in interstitial DOC concentration in peat under burns in well-managed rotations (i.e. burned every ten years), and Worrall *et al*. (2007) found DOC concentrations to be lower under those circumstances. While this might be considered contrary to the data presented here, it should be noted that both of these studies relate to burns at the end of the ten year cycle that had already recovered to full canopy. These correspond to Class 3 and Class 4 burns as described here, and in this research no such relationship was observable either, implying that the phenomenon of enhanced DOC release as a consequence of fire management is time-limited to a period of less than ten years. Clay *et al*. (2009) monitored DOC concentration for the year following a controlled 'cool' burn, but also found no significant difference in DOC concentration in interstitial water or surface water runoff. However, it must be noted that Clay *et al*. (2009), Ward *et al*. (2007) and Worrall *et al*. (2007) did not measure DOC concentration in drainage water as examined here, and although it might be assumed that DOC concentrations in interstitial and drainage water from blanket peat might be linked (Clark *et al*., 2008), this is not necessarily so. If infiltration and throughflow is greater under new burn patches as identified by Imeson (1971), this could suggest a more constant renewal of interstitial water, which would maintain lower interstitial DOC levels as observed by Worrall *et al*. (2007) from continued dilution or 'flushing'. The accumulation of decomposition products have been linked as an inhibitory factor limiting peat decomposition (Freeman *et al*., 2001b) suggesting that high interstitial DOC levels could in fact potentially inhibit overall productivity, albeit with apparently higher 'standing concentrations'. Lower interstitial DOC concentration could therefore be indicative of higher overall productivity in well flushed systems with concomitant high levels in drainage waters.

Further difference between previous studies and the data presented here may arise from the style of burn management implemented. Clay *et al*. (2009) report the burning style adopted at Moor House to be of controlled ‘cool’ burns on ten year old vegetation, with no visible evidence of scorching or combustion of the peat or litter layers. Studies of the dynamics of heath fires indicate that temperature and fire intensity increase with stand age, related to the amount of fuel available (Hobbs and Gimingham, 1984a). Above ground biomass of *Calluna* approximately doubles every 10 years after burning up to a maximum 30-40 years (Hobbs and Gimingham, 1987). The expansion of burning into areas of blanket peat over the last 40 years (Figure 7.3.12) clearly shows that areas of *Calluna* dominated moorland that have not been visibly ‘managed’ since at least the 1960s are now under active burn management. It is reasonable to assume that the temperature of burns in these areas would be hotter than those at Moor House due to the age of stands being burned. As a result of increased temperatures that occur during burning of very old stands, regrowth of vegetation is extremely slow and often reliant upon germination from seeds, which leaves ground bare for many years after the fire (Hobbs and Gimingham, 1984b). This is highlighted by observations in this research that five to six years after a burn event, some 40% of the peat surface is still exposed in some burn scars (Chapter 4.3.3).

9.3. Limitations and recommendations for future research

The research presented in this thesis has focussed on upland peat catchments in the South Pennines and North Yorkshire Moors, and provides convincing evidence that controlled burning significantly enhances DOC production in blanket peat soils. In the English uplands some 114 km^2 of controlled moorland burn occurs annually (Yallop *et* *al*., 2006a), a figure that could have significant consequence for blanket peat soils nationally. However, the response of blanket peat soils to controlled burning in other areas of the UK could be significantly altered by climatic conditions, vegetation communities and rates of burn recovery/re-vegetation. Although the spatial constraint imposed upon the selection of catchments used in analysis here reduced the potential variability in climatic factors and vegetation communities, thereby allowing the effect of extrinsic factors to be assessed, it is likely that there is reduced variability in the application of land management. Areas of heather moorland in the study areas are predominantly managed for red grouse, and therefore there was little opportunity to assess DOC concentrations in drainage water from unmanaged blanket peat catchments. A key area for future research is to understand how the effects of burning vary over greater spatial extents within the UK, and also include of areas of unmanaged heather moorland.

The constrained spatial extent of the study area may also have reduced the variability in soil types between study catchments, which is important as the analysis presented here assumes that the areas of blanket peat identified from digital soil data (map unit 1011b; Mackney *et al*., 1983) are homogenous across the study area. However, map unit 1011b is defined as being “at least 30cm deep” (Burton and Hodgson, 1987), but in some upland areas blanket peats may be up to 6-7 m deep (Charman, 2002). Owing to the extent of the area, it was not possible to survey peat depth across the study catchments, and it is not clear whether peat depth might influence the hydrological response of blanket peat to external factors such as land management. It is suggested that peat depth should be included in subsequent research, and where possible include collation of additional soil data at a finer resolution than current digital soil data.

Assessment of the extent of burn management in the catchments examined in this research was limited to those years where aerial photography was available. This precluded the opportunity to assess the interaction between extrinsic factors and burning on DOC production. To fully understand these interactions requires experimental manipulation and this is a further key area that requires investigation. The approach of experimental manipulation would also enable further development of understanding the effects of burning on carbon loss from peatlands via other fluvial and gaseous release pathways and improve our understanding of the implications of burning management on national carbon budgets.

Determination of DOC flux from WTW data was speculative, requiring the modelling of runoff behaviour and estimation of catchment runoff from rainfall volumes. That the flux estimations lie within the range of figures published for other studies in the UK suggests that the figures presented here may provide reasonable representation. However, validation of the modelled fluxes was not possible owing to the lack of stream flow data. WTW data provide long-term historical records of fluvial carbon loss and these data should be used in further research. To improve estimations of DOC flux and allow assessment of error, it is suggested that rainfall and stream flow for the catchments supplying the WTW be monitored to allow better modelling and validation of runoff behaviour.

The comparison of the results of DOC assessment studies assumes that the composition and source of 'DOC' measured in all studies is the same. In this research, measured DOC is inferred to have derived from the decomposition of blanket peat. The strong linear relationship identified between Hazen and DOC for the 50 small headwater catchments (Chapter 5) indicates that this is applicable to the environments examined here and allowed the estimation of humic DOC (hDOC) concentration from water utility data. The terms 'DOC' and 'hDOC' may allow better discrimination between studies, particularly where 'DOC' may contain anthropogenic input in lower order streams (Tipping *et al*., 1997; Eatherall *et al*., 2000) or the products of plant decomposition from early stages of decay (Palmer *et al*., 2001). Fractionation of DOC could provide better understanding of the origins of the carbon measured and is perhaps, therefore, the most important theme for further study highlighted by this research.

This thesis provides a valuable contribution to understanding the effects of localised activities on peatland carbon cycling, and it is hoped that this insight will assist future decisions concerning upland catchment management. DOC concentrations in surface waters appear to have been significantly increased by changes in land management policy, and this knowledge could provide great benefit for water utility companies, and conservation of blanket bog environments. Several key areas for future research have been highlighted.

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